Chapter

1

Introduction:

1.1 Background:-

Carbon dioxide gas (CO_2) is a natural, fluctuating component of earth's atmosphere and has been present throughout most of geological time. The climate change is the biggest environmental challenge, world is in front of today. To avoid synthetic climatic changes it is necessary to lessen the **Carbon dioxide** (CO_2) emission significantly. Given the advantages innate in fossil fuels; such as their availability, relatively low cost and the existing infrastructure for deliverance and circulation, they are likely to play an important role in the world wide energy production for at least next 75 years. Therefore there is also an increasing interest in CO_2 capture, storage and utilization [1].

Carbon dioxide is the major cause of the climatic changes occurring in the atmosphere of the universe. The distinguishing properties like Green house properties and incessant accumulation in the atmosphere make Carbon dioxide a continuous danger for the atmosphere.

1.2 Carbon Dioxide Emission:-

The CO_2 atmospheric concentration has increased from 278ppm during the preindustrial era to current level of 387ppm (Figure 1.1) [2].This increase in the concentration of carbon dioxide in atmosphere is mainly because of industries, transportation and human activities like burning of fossil fuels, deforestation and other issues including incenirstion of waste, landfills and Agricultural soil management.Carbon dioxide relaeased into the atmosphere primarily comes through the use of fossil-fuels which are currently our main energy source. This raise of CO_2 loadings in atmosphere leads to ecological and social changes.Most of the observed increase in global average temperature since the mid-20th century is very likely due to the increase in the concentration of green house gases in the atmosphere, out of which Carbon dioxide gas is the major one. Projections of the future climatic change suggest further global warming, sea level rise and increase in the frequency of some extreme weather events. Proof of climatic changes includes instrumental temperature records, rising sea levels and decreased snow thickness in the northern hemisphere.

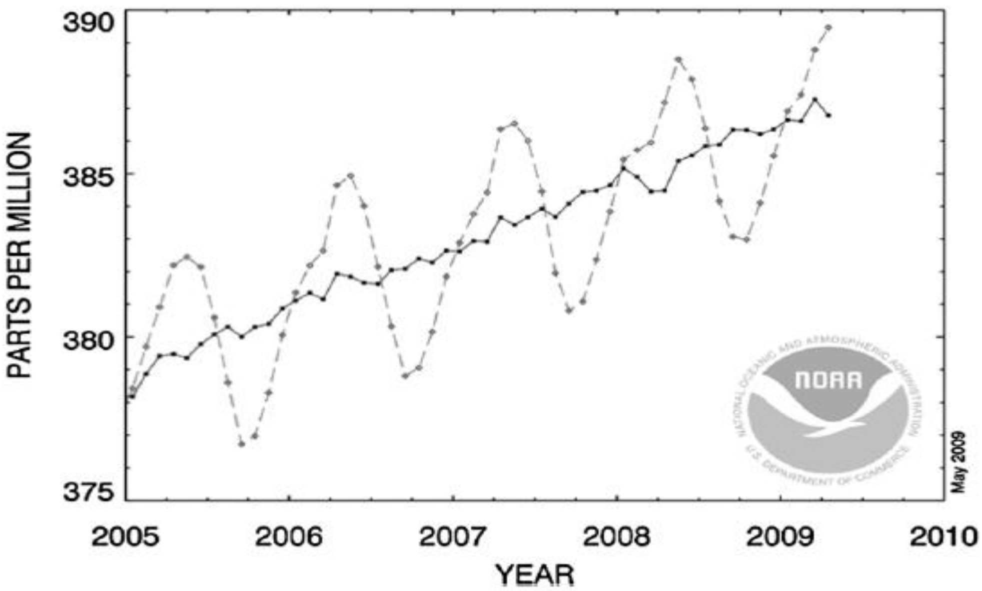


Figure 1.1 The steady increase in CO_2 concentrations in recent years [2].

Since the Industrial Revolution, anthropogenic activites like burning of oil, coal and gasalong with the issue of deforestation have made the concentration of carbon dioxide CO_2 in atmosphere greater than before. Types of fossil fuels that are used the most include coal, natural gas and petroleum. Upon combustion of these the carbon stored in them is almost entirely emitted as Carbon dioxide CO_2(Figure 1.3).The origin of this huge emission of CO_2 and of its sound addition in the atmosphere,has been the use of Carbon-based fossil fuels in human activities (Figure 1.2) [3].

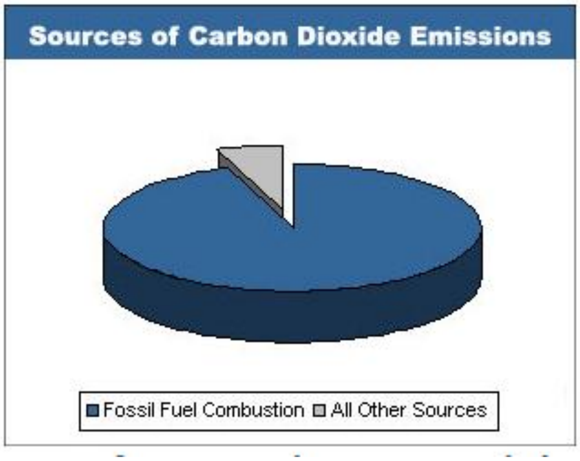


Figure 1.2 Carbon dioxide's emission through fossil fuels and other sources[3].

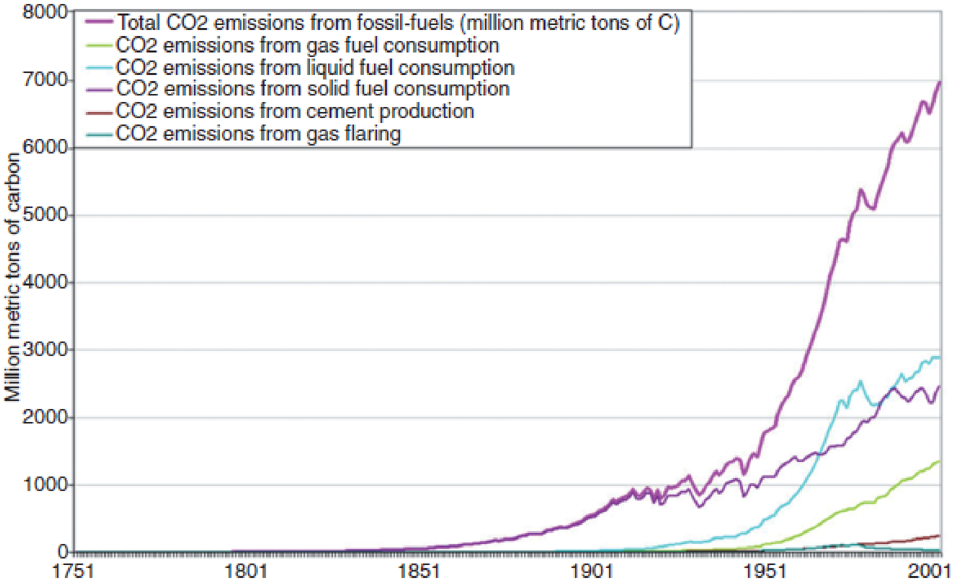


Figure 1.3 The origin of emission of CO_2[2]

1.3 The Accumulation of CO_2 in the Atmosphere and the Effects that We Fear:-

Today, the increasing concentration of carbon dioxide in the atmosphere is adversly affecting the atmosphere. Serious concerns are being raised regarding the influence of CO_2 on climatic changes.

Almost 100% of the observed temperature increase over the last 50 years has been due to increase in concentration of green house gas is water vapours, carbon dioxide CO_2, methane and ozone in the atmosphere. The largest contributing source for the green house effect is burning of fossil fuels that result in the emission of carbon dioxide CO_2. Many compounds present in the Earth's atmosphere act as "green house gases." Some of them are natural (water vapour, carbon dioxide, methane and nitrous oxide) while rest are anthropogenic (CF_4, C_2F_6, C_3F_8, SF_6 gases used for aresols).

The green house effect that is associated with the energy production and use- whether by the direct relaease into the atmosphere of flue gas associated heat production by the energy, industrial, and transport sectors or by the emission of green house gases (see next section) – is slowly causing in rise of the earth's temperature. As revealed in a report by the

Intergovernmental Panel on Climate Change (IPCC) (Figure 1.4)[2]. These changesin the thermal structure of atmosphere on the Earth's solid surface area causing the temperature of the planet's water to rise and there volume to increase to a point where the rising water level on the Earth's surface are seen as a major problem, specialy in coastel areas.

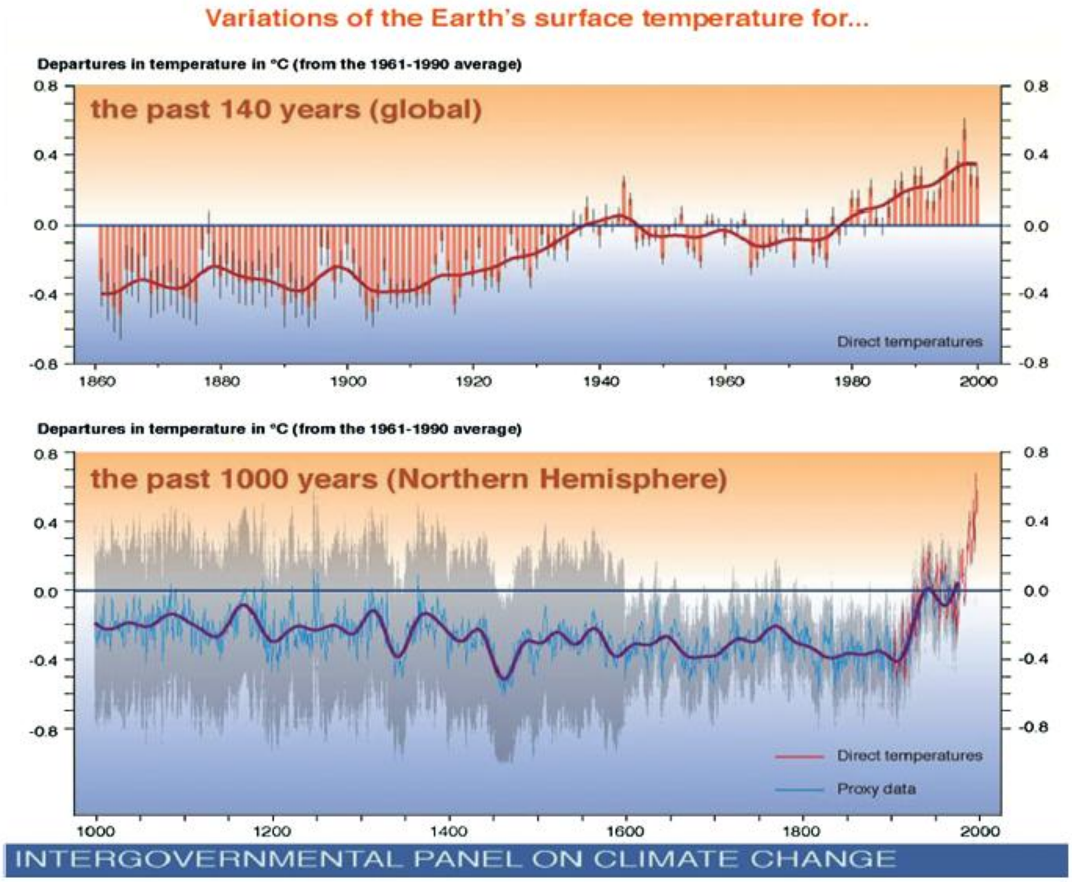


Figure 1.4 Variation of temperature of Earth during last millenium (IPCC data)[2]

1.4 Green House Effect:-

The **greenhouse effect** is the warming of the atmosphere by the trapping of long wave radiation being radiated to space [4]. The thermal radiation from an earthly surface is engrossed by the atmospheric greenhouse gases (water vapours, carbon dioxide, methane, nitrous oxide etc), and is re-radiated in every direction. Since fraction of this re-radiation is back towards the surface, energy is transferred towards the surface and the lower atmosphere. Consequently the average surface temperature is higher than it would be if the direct heating by solar radiation were the only warming mechanism.

Solar radiation at the high frequencies of visible light enter the atmosphere to heat up the planetary surface, which then emits this energy at the lower frequencies of infrared thermal radiation. Infrared radiation is absorbed by the greenhouse gases, which in turn re-radiate much of the energy to the surface and lower atmosphere. The mechanism is named after the effect of solar radiation passing through glass and warming a greenhouse nursery, but the way it retains heat is fundamentally different as a greenhouse work by reducing airflow, isolating the warm air inside the structure so the heat is not lost by convection.

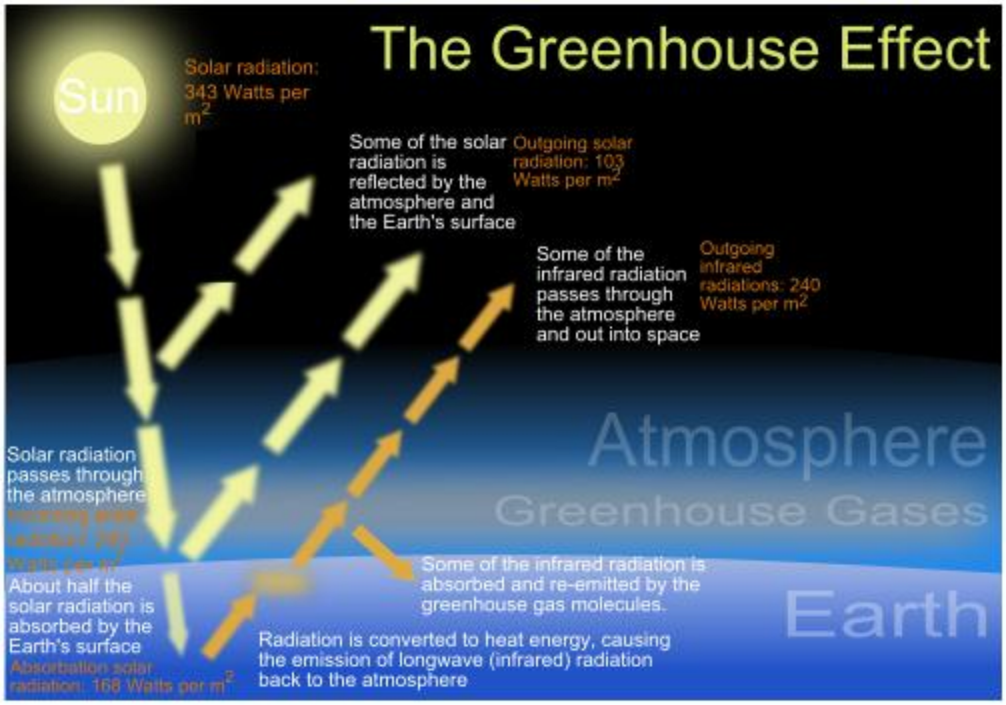


Figure 1.5 The Green house Effect[4].

1.5 Green House Gases:-

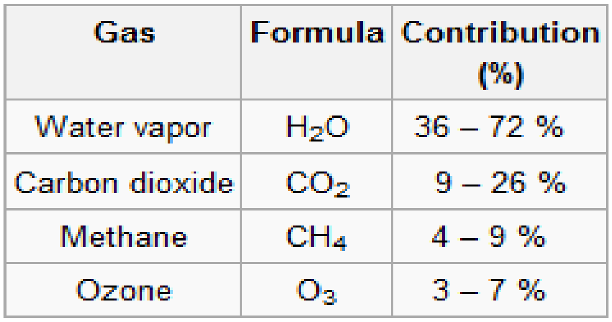
Greenhouse gases can absorb and emit infrared radiation. The most abundant greenhouse gases in Earth's atmosphere are:

- water vapor
- carbon dioxide
- methane
- nitrous oxide

- ozone

When these gases are ranked by their direct contribution to the greenhouse effect, the most important are:

Table 1.1 Table showing the contribution of main Green House Gases [5]



Gas	Formula	Contribution (%)
Water vapor	H_2O	36 – 72 %
Carbon dioxide	CO_2	9 – 26 %
Methane	CH_4	4 – 9 %
Ozone	O_3	3 – 7 %

In addition to the main greenhouse gases listed above, other greenhouse gases include sulfur hexafluoride, hydro fluoro carbons and hydrofluoro carbons and perflurocarbons. Some greenhouse gases are not often listed. For example, nitrogen trifloride has a high global warming potential (GWP) but is only present in very small quantities.

1.6 Carbon dioxide Capturing Technologies:-

CO_2 capture is the process of removing CO_2 (carbon dioxide) produced by hydrocarbon combustion (coal, oil and gas) before it enters the atmosphere. The process will be most cost effective when it is used on large point sources of CO_2 such as power stations and industrial plants. These currently make up more than half of all man-made CO_2 emissions.

CO_2 capture is an existing industrial technology widely used, on a smaller scale, in the manufacture of fertilizers, the food-processing industry and within the oil and gas sector. The main challenge for any capture process is the low concentration of CO_2 in the flue gas. Depending on the industrial source CO_2 content can vary from a few percent to well over fifty percent. Other contaminant gases such as oxygen, sulphur oxides, water vapor and nitrogen can also be present in flue gases. For reasons of both economic and energy costs it would be impossible to compress and store all of them. Therefore CO_2 must be preferentially separated from the other flue gases by a capturing process.

As mentioned earlier, we will remain dependent on fossil fuels for the upcoming decades as they are the only long lasting energy source yet available. This means that CO_2 emission will continue to rise which ultimately has adverse effect on the climate. These emissions from different sources have increased its concentration in the atmosphere. It has to be stabilized so that anthropogenic disturbance in the climate system can be prevented.

To reduce these emissions, different CO_2 capturing technologies can be employed. CO_2 can be disposed off deep under the sea using a long pipe line or with the help of ships, as well as stored at geological formations deep under the ground. This kind of storage is also used commercially to enhance the flow of crude oil from its source and is therefore not restrained from the atmosphere. Captured CO_2 can also be used for some industrial purposes. It is used in gaseous or liquefied state as feed stock in chemical processes that produce valuable carbon containing product. Several different methods have been proposed for how to perform CO_2 capture from power plants, but the maturity of the technologies differs. The most mature technology is the post-combustion method including amine absorption. The major problem using this technology has been the high operational cost, mainly due to the regeneration of amines. Carbon dioxide capturing technologies can be classified in three different categories, depending on the location where the capture actually take place;

1. Pre-combustion capture
2. Oxy-fuel combustion
3. Post-combustion capture

1.6.1 Pre-combustion Capture:-

Pre-combustion capture involves removal of CO_2 prior to combustion, to produce hydrogen. Hydrogen combustion produces no CO_2 emissions, with water vapor being the main by-product. Provided that this technology is used with carbon storage it could provide a CO_2 emission free fuel for the future.

The capture process consists of three stages; firstly the hydrocarbon fuel (typically methane or gasified coal) is converted into hydrogen and carbon monoxide (CO) to form a synthesis gas.

The second step is to convert the CO into CO_2 by reacting it with water and which is known as shift conversion. Finally, the CO_2 is separated from the hydrogen which can then be combusted cleanly. The CO_2 can then be compressed into liquid and transported to a storage site.

Pros:

- Proven industrial scale technology in oil refineries, but needs 3x scale-up for power plants.
- 90-95% of CO_2 emissions can be captured.
- Applicable to natural gas and to coal fired IGCC power plants.
- Lowest technology risk, and may become the most efficient method.
- Can produce H_2 as transportable energy vector, or liquid fuels from coal - but penalties on efficiency.

Cons:

- Requires a chemical plant in front of gas turbine.
- High investment cost of dedicated new-build plant.
- High NOx emissions – will require expensive scrubbers.
- Efficiency of H_2 burning turbines is lower than conventional turbines.
- May be less flexible under varying electricity generation market requirement, so base load preferred.

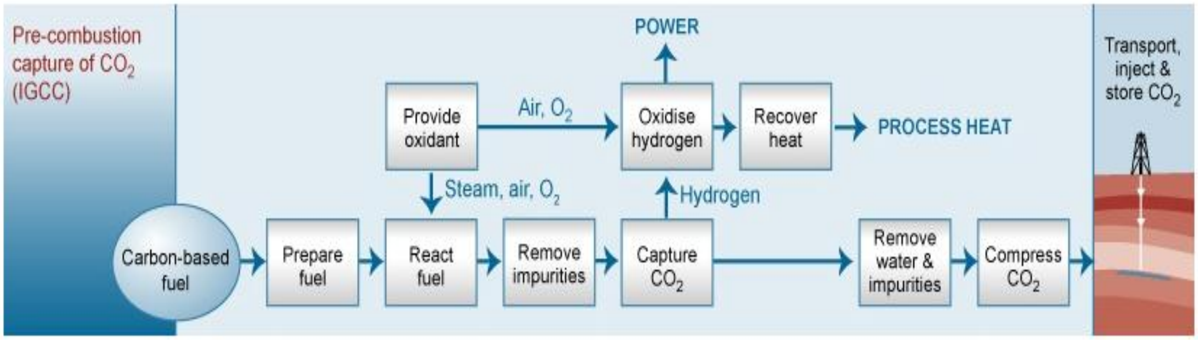


Figure 1.6 Pre-combustion capturing of Carbon dioxide[6].

1.6.2 Oxy-fuel Combustion Capture:-

This process involves burning fossil fuels in pure oxygen as opposed to air resulting in a more complete combustion. This results in an exhaust stream which consist of almost pure CO_2 (typically ater vapor, which can be easily separated from the CO_2 by condensation.

The main problem with this method is separating oxygen from the air. This is usually completed cryogenically which requires a lot of energy (for a typical 500MW coal-fired power station supplying pure oxygen requires at least 15% of the electricity the plant generates annually). However, a promising new technology called chemical looping combustion is under development. With this technique the oxygen in the air is removed by oxidation of a metallic compound which can be reduced during combustion allowing the oxygen to be released.

Pros:

- Potential for 100% CO_2 capture.
- Few other harmful emissions due to more complete combustion.
- May be possible to retro-fit the oxy-fuel burners onto modified existing coal power plant

Cons:

- High energy penalty without chemical looping combustion.
- Only at large development stage at present - first demonstration plants recently commenced operation.

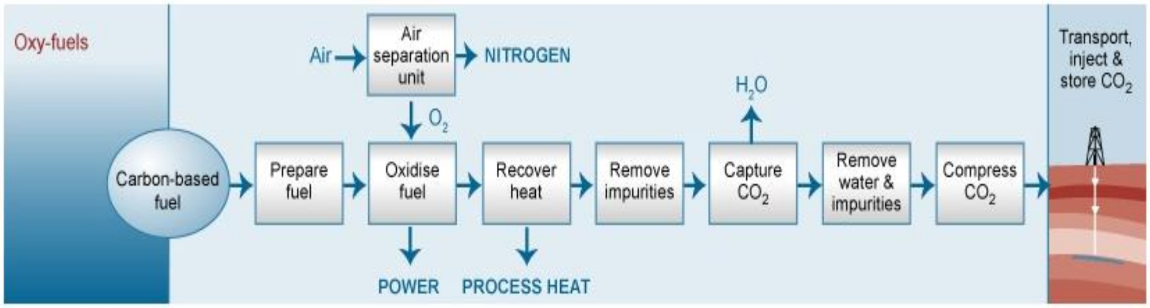


Figure 1.7 Oxy-fuel combustion capturing of Carbon dioxide[6].

1.6.3 Post-Combustion Capture:-

Post-combustion capture involves removing the dilute CO_2 from flue gases after hydrocarbon combustion. It can be typically built in to existing industrial plants and power stations (known as retro-fitting) without significant modifications to the original plant. This is the type of technology favored by tech UK Government in its competition for state support.

There are several methods that can be used to capture the CO_2. The most common method is passing the CO_2 through a solvent and adsorbing it and amine solvents are typically used. A change in temperature and/or pressure will then release the CO_2. Another process in development is calcium cycle capture where quicklime is used to capture the CO_2 to produce limestone, which can then be heated to drive off the CO_2 and quicklime which can then be recycled. All of these require additional energy input to drive off the CO_2 from the solvent - this typically results in extra energy costs of 20-30% compared to plants with no capture. New solvents are under development to reduce these penalties to 10%.

Other post-combustion possibilities, currently being researched, include cryogenically solidifying the CO_2 from the flue gases, or removing CO_2 with an adsorbent solid, or by passing CO_2 through a membrane.

Pros:

- Feasible to retrofit to current industrial plants and power stations.
- Existing technology - 60 years' experience with amine solvents - but needs 10x scale-up.
- Currently in use to capture CO2 for soft drinks industry.

Cons:

- High running costs – absorber and degraded solvents replacement.
- Limited large scale operating experience.

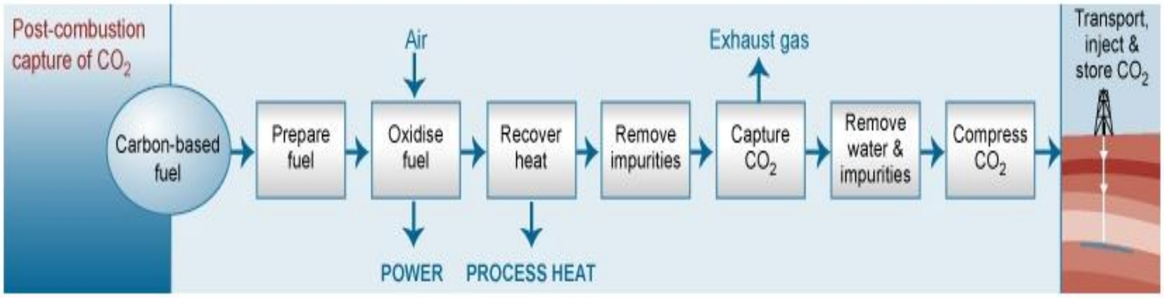


Figure 1.8 Post-combustion capturing of Carbon dioxide$_{[6]}$.

1.7 Utilization of Carbon Dioxide:-

The use of CO_2 (biological/chemical/technological) is the only tool that may contribute in sinking the atmospheric loading while generating a profit. Of course it would be far better if the unnecessary by-product could be renewed into a green and profitable product. Nature utilizes CO_2 to produce innumerable substances that are consumed by humans and animals. Some industrial processes aim to accelerate the utilization of CO_2.

There are essentially three pathways for utilizing CO_2 [7].

- Conversion of CO_2 into fuel
- Utilization of CO_2 as a feedstock for chemicals
- Non-conversion use of CO_2

The various utilization technologies together have the potential to reduce CO_2 emissions by at least 3.7 giga tons/year (Gt/y) (approximately 10 % of total current annual CO_2 emissions), both directly and by reducing use of fossil fuels. However, much greater reductions are possible through wider adoption of these technologies [7].

Biochemical or chemical conversion of CO_2 to fuels using biomass is an attractive technology for converting large quantities of CO_2 into readily practical chemicals. Only 5 % of liquid fossil fuel be replaced by biomass-based liquid fuel, then, based on a variety of lifecycle CO_2 emissions, a decline of approximately 0.4 Gt/y of CO_2 would result. CO_2conversion to minerals and introduction into polymers may have the advantage of sequestering CO_2 in relatively stable matrices. If 10 % of global building material demand was met by transfer of CO_2 to stable minerals, then a potential reduction of 1.6 Gt/y of CO_2 has been predictable. Chemical and electro-chemical conversion of CO_2 into value-added chemical feedstock and intermediates is attractive in terms of fossil fuel avoidance. It is estimated that the total CO_2 emissions avoidance potential of this path way is about 0.3 Gt/y. The non-conversion uses of CO_2, such as enhanced oil recovery and solvent use, have the potential to consume about 1.4 Gt/y of CO_2.There is no single, universally applicable pathway for CO_2 utilization. Depending on the industry, location, and other constraints, one or more technologies may fit better than others. An approach that integrates different methods may be the most practical solution for many applications. CO2 can be utilized in three major pathways :

1. As storage medium for renewable energy
2. As a feedstock for various chemicals
3. As a solvent or working fluid.(Figure 1.10)

The use of CO_2 to convert solar energy into biomass and, from there, to various renewable fuels is now widely supported by industry and governments as a means to secure future energy supplies and to decrease net CO_2emissions to atmosphere. It has been estimated that by 2035, the world will produce15 Gt/y of CO_2 from burning liquid fuels [8]. Therefore, replacing about 5 % of liquid fuels with bio-fuel, and assuming a 50 % lifecycle reduction in CO_2 emissions in comparison with petroleum-based fuel, has the potential to reduce CO_2 emissions by 0.4 Gt/y. In addition to generating biomass, CO_2 can be converted via chemical and electrochemical processes to other energy storage chemicals, such as syn-gas, formic acid, methane, ethylene, methanol, and dimethyl ether (DME).

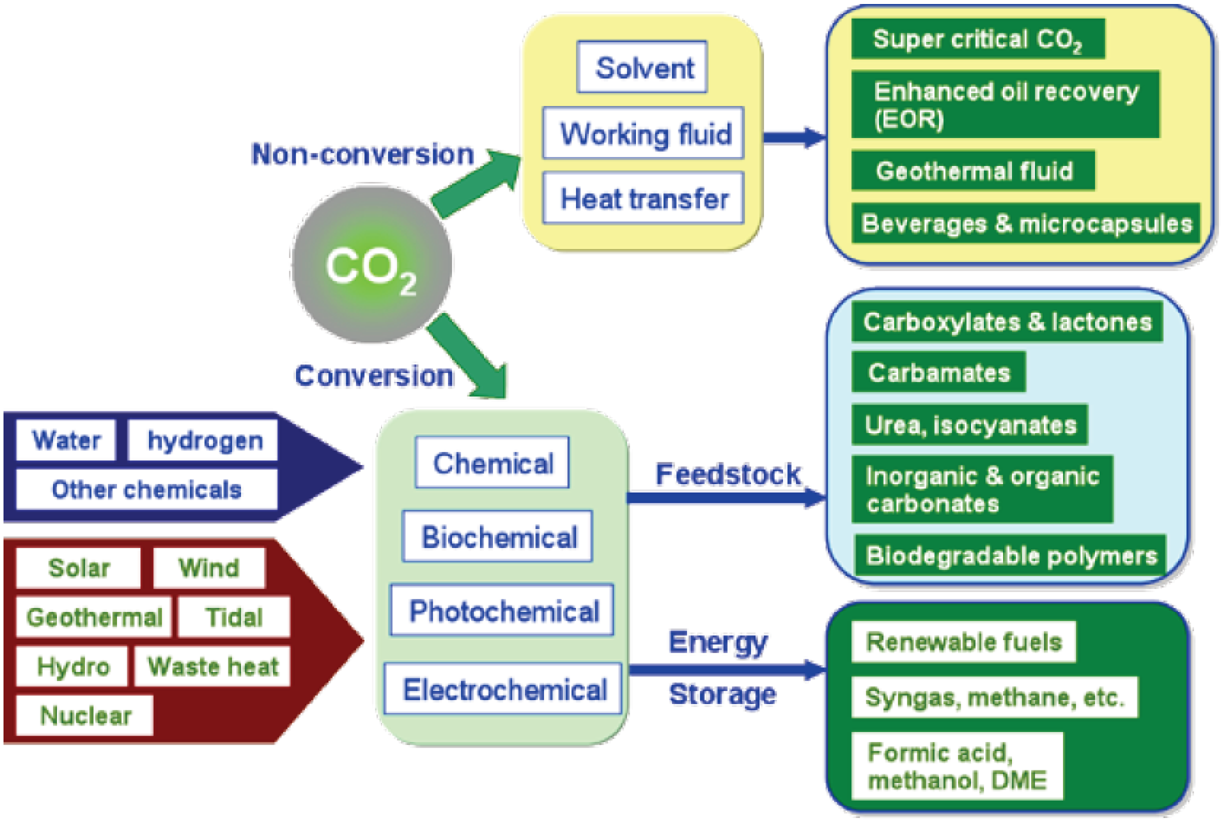


Figure 1.9 Different pathways for utilizing CO_2 [8].

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[2] Michele Aresta, Carbon Dioxide: Utilization Options to Reduceits Accumulation in the Atmosphere

[3] Inventory of U.S. Greenhouse Gas Emissions and Sinks (2008), EPA.

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Chapter 2

Literature Review:

The utilization of CO_2 as a source of carbon for the synthesis of different chemical products is considered with increasing interest. New synthetic processes using carbon dioxide have been discovered. Some of them may be developed at the universal level if suitable economic conditions were created. The development of chemical industry based on CO_2 would have the following positive consequences:

- Solving the problem of atmospheric CO_2 level
- Avoiding the use of toxic material in some industrial processes
- Substituting CO_2 to fossils (coal, oil, gas) as a source of carbon for some industrial applications
- Saving energy by recycling carbon
- Using safe solvents
- It is necessary to synthesize products with the market of several million tons per year and requiring low energy input. Products with a long life appear quite attractive. The correct evaluation of the contribution that a synthetic procedure based on CO_2 can give mitigation of CO_2 or to the development of "green industry", requires a complex analysis based on criteria listed below:
- Added value of product
- Market demand of the product
- Demand of energy for the product
- Life of the product
- Transformation rate of CO_2 (yield & selectivity towards the product)

2.1 Synthesis of fuels, intermediates and different fine chemicals:-

CO_2 can be fixed in chemical substance:

- As it is; like carboxylates (RCOOR), carbonates (ROCOOR) and polycarbonates, carbamates (RR'NCOOR) and polyurethanes, urea and their derivatives.
- In a reduced form; like CO, CH_2O, CH_3OH or the homologous species C_n and their derivatives.

2.2 Synthesis of Various Chemical Compounds Using CO_2:-

2.2.1 Synthesis of Methanol CH_3OH:-

Methanol can be produced by the reaction of CO_2 with Natural gas (CH_4) and steam.

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CH_3OH$$

The synthesis of methanol deserves attention; this product can be used as fuel or as a raw material for the synthesis of chemicals. The conversion of CO_2 into methanol requires dihydrogen (H_2).

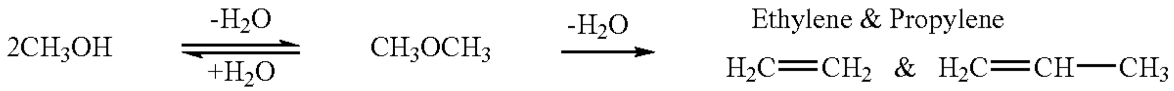
$$CO_2 + 3H_2 \longrightarrow CH_3OH + H2O$$

This approach can result of great interest if a cheaper and easier conversion of water into hydrogen were found. Its different uses are:

a. Anti-freezing agent
b. Paint industry
c. Rubber synthesis
d. Semiconductor
e. Wood stain and varnishes
f. Paper coating
g. Pesticides manufacturing
h. Pharmaceuticals manufacturing
i. Solvent

Various chemical are produced using methanol like Dimethyl ether, Ethylene, propylene and biodiesel etc.

$$3CH_4 + 2H_2O + CO_2 \longrightarrow \underbrace{4CO + 8H_2}_{4CH_3OH} \longrightarrow 2CH_3OCH_3 + 2H_2O$$



$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \overset{\text{Ethylene \& Propylene}}{H_2C{=}CH_2 \;\&\; H_2C{=}CH{-}CH_3}$$

Figure 2.1 Production of Hydrocarbons using CO_2

Methanol along with Dimethylether is an excellent fuel. It is particularly effective fuel for diesel engines because of its high cetane number and favorable combustion properties. Methanol and Dimetylether exceedingly blend with diesel oil to be used in internal combustion engines or electricity generators. One of the most efficient uses of methanol is fuel cells. Contrary to gasoline, which is a complex mixture of various hydrocarbons methanol is single simple chemical compound, it contain about half the energy density of gasoline.

Methanol is one of the safest fuels available. Compared to gasoline, methanol's physical and chemical properties significantly reduce the risk of fire. Methanol is also an attractive liquid fuel for static applications. For example methanol can be used directly as a fuel in a gas turbine to generate electricity.

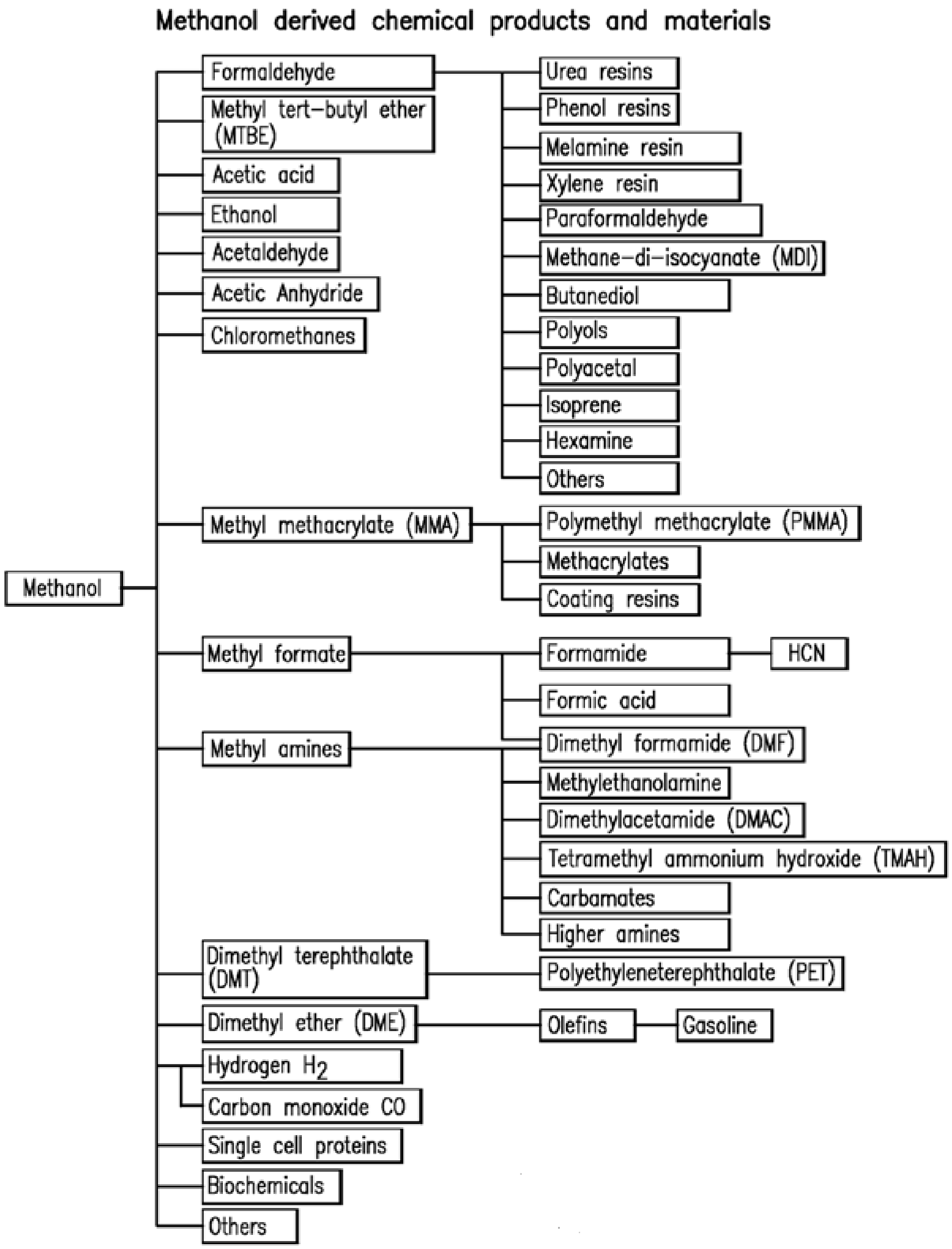


Figure 2.2 Uses of Methanol

2.2.2 Formic Acid Synthesis from CO_2 Hydrogenation:-

$$CO_2 + H_2 \longrightarrow HCOOH$$

Formic acid can be prepared by the hydrogenation of CO_2. In the reaction the CO_2 can be obtained from various industrial waste and H_2 from the electrolysis of water. Although it has limited industrial uses but it is high volume chemical with production exceeding1 million pounds annually in USA. It is used in:

a. Electroplating
b. Leather industry
c. Reprographic agent
d. Printed circuit board manufacturing

2.3 Conversion of Carbon Dioxide to Valuable Petrochemical:-

Carbon dioxide has already been used in petrochemical industry for the production of limited chemicals.

$CO_2(g) + H_2(g) \rightarrow HCOOH(l)$

$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l)$

$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(l)$

$CO_2(g) + CH_4(g) \rightarrow CH_3COOH(l)$

$CO_2(g) + CH_4(g) + 2H_2(g) \rightarrow (CH_3)_2CO(l) + H_2O(l)$

$CO_2(g) + H_2C = CH_2(g) \rightarrow H_2C = CHCOOH(l)$

An immediate and effective solution for the utilization of CO_2 is its conversion to more reactive carbon dioxide via a reverse water gas shift (WGS) reaction.

$CO_2+H_2 \Leftrightarrow CO+H_2O$

Development of new chemical processes for chemical fixation of CO_2 to produce alcohol, ether and hydrocarbons supplies new feed stock for the synthesis of petrochemicals and fuels.

2.3.1 Steam Electrolyser for the Joint Electro-Reduction of CO_2 and CO for the Production of Hydrocarbons:-

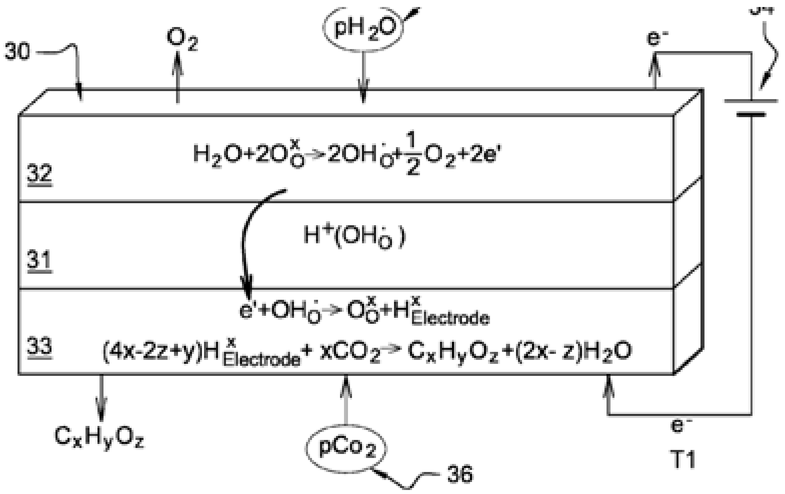


Figure 2.3 Steam Electrolyser

Where

32 is ***anode,*** where water is oxidized to produce proton H^+ and O_2

31 is ***electrolyte (proton or ion conductor),*** which conduct H^+ ion

33 is ***cathode,*** where H^+ reduces the CO or CO_2 to the desired chemical

And $C_xH_yO_z$ are different hydrocarbons formed accordingly.

2.4 Photo-electrochemical Approach for the Chemical Recycling of CO_2 to Fuels:-

There is an opportunity to recycle CO_2 back to liquid fuels, by using a novel Photo-Electro Chemical (PEC) approach integrated with utilization of nano-sized material as photo-electro catalysts. The PEC reactor developed for H_2 production by water photo electrolysis can ideally be adopted for gas phase reduction of CO_2 to fuels. Photo-reactor working like a reverse fuel cell is used for the purpose and is configured in the manner to minimize the light scattering phenomena and increase the photo efficiency of the process. Results, obtained separately from experiments with the photoanode (H_2 production from solar light) and the electrocathode (CO_2 reduction by current application), are very promising for the future application in chemical recycling of CO_2, as a complementary technology to carbon sequestration and storage.

Figure 2.4 Photo-electrochemical recycling of CO_2

2.4.1 Structure:-

The photo-anode is a nano-structured TiO_2 thin film supported over a porous Titanium foil. The cathode consists of Pt or Fe/ Carbon nanotubes (CNT) supported on carbon cloth (CC). The two electrodes are joined together by protonic membrane (Nafion).

2.4.2 Working:-

- Light crosses the quartz window and reaches the nano structured film (photoanode) where photo generated electron and hole pairs are generated and O_2 evolves,
- Proton pass through the protonic membrane, while electrons are collected and reached the cathode through the external wire,
- Protons react with CO_2 in the presence of electrons on the CNT based electrocatalyst to give liquid fuels, or combine with electrons over Pt nanoparticles supported on carbon cloth to give H_2.

The physical separation of the two reactions of water oxidation and CO_2 reduction in a photoanode and electrocathode respectively, is necessary to increase the efficiency of the process and limit recombination. This device could be used to produce renewable hydrogen by photo catalytic reforming of chemicals present in waste streams of agro-food or agro-chemical production, such as diluted streams of ethanol, glycerols etc.

2.5 Grignard’s Reaction:-

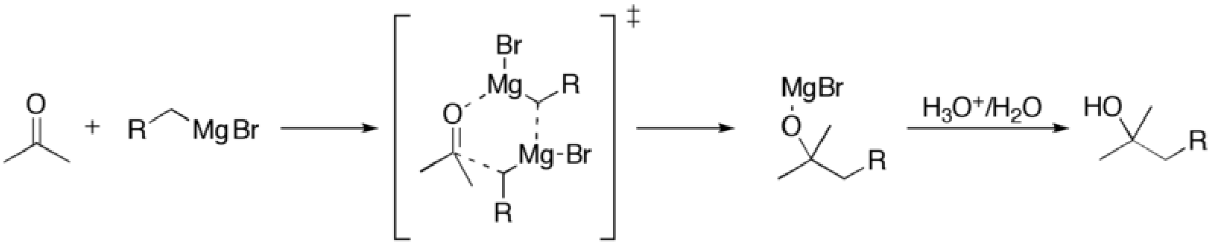
The Grignard Reaction is an organometallic chemical reaction in which alkyl or aryl magnesium halides add to a carbonyl group. Grignard’s reaction plays an important role in the formation of Carbon – Carbon bonds.

2.5.1 Grignard's Reagent:-

Grignard reagent is a chemical compound with formula **RMgX** Where **R** represents the organic part of the compound. It may be any alkyl or aryl (based on benzene ring) group and **X** represent the Halogen family.

2.5.2 Reaction Mechanism:-

Grignard reagent plays the roles of nucleophiles attacking electrophilic carbon atomthat are present within the polar bond of the Carbonyl group. Reaction mechanism can be represented as



2.5.3 Preparation of Grignard Reagent:-

Grignard reagent is formed by the reaction of alkyl or aryl halide with Magnesium metal in a moisture free atmosphere. Ether or Tetra Hydro furan is mainly used as solvents and they provide ligands for the stabilization of organo-magnesium compound formed. The overall reaction proceeds at the surface of magnesium metal being used.

The reaction proceeds through Single electron transfer and the radicals formed can be converted into Carbanions through second electron transfer mechanism.

$$\mathrm{R{-}X + Mg \rightarrow R{-}X^{\bullet -} + Mg^{\bullet +}}$$
$$\mathrm{R{-}X^{\bullet -} \rightarrow R^{\bullet} + X^{-}}$$
$$\mathrm{X^{-} + Mg^{\bullet +} \rightarrow XMg^{\bullet}}$$
$$\mathrm{R^{\bullet} + XMg^{\bullet} \rightarrow RMgX}$$

Above chemical reaction represent the general mechanism for the preparation of Grignard reagent. However commercially available Grignard reagents can also be utilized for experimental purposes.

2.5.4 Reaction Conditions:-

In reaction involving Grignard reagents removal of water and air is the most important issue as these can destroy the reagent by protonolysis or oxidation reaction. That’s the reason that the reactions are carried out in anhydrous diethyl ether or tetra hydrofuran as the possibility of side reactions are limited by the protective blanket provided by solvent vapors.

The apparatus must be dried before use to avoid further side reactions. It’s better to use nitrogen or argon atmosphere while working at lab scale.

2.5.5 The Organic Halides:-

Grignard reaction often starts slowly. For the reactions involving solution and solid, there is an induction period during which reactive magnesium is exposed to organic reagent. After that induction period the main reaction occurs that may be highly or moderately exothermic. Alkyl and Aryl **Bromides** and **Iodides** are common substrate. Chlorides are also used but Florides are rarely used as they are unreactive.

2.5.6 Magnesium:-

Typically magnesium ribbons are used for the Grignard reaction. All magnesium is coated with a layer of magnesium oxide, which hinders the reaction of organic halides with reactive magnesium. For the mentioned reason specially activated magnesium can be used or there are certain methods for the activation of oxidized magnesium ribbons or turnings. Specially activated magnesium, such as Rieke magnesium is available in market and can efficiently circumvents this problem.

2.5.7 Solvent:-

Ethereal solvents are mainly used during the Grignard reaction conduction, especially Diethyl ether (commonly known as ether) and Tetra hydrofuran (THF).

2.6 Applications of Grignard's Reagent:-

The most common application of grignard's reagent is for the alkylation of aldehydes and ketones.

- **Chemical Industry**
    - Grignard reagent is used in Alkylation, in coupling reactions, for making Esters having different Functional Groups, Aromatic & Tertiary Thiols etc.
- **Industrial Applications**
    - The reagent is mainly used in the Organic chemistry, particularly for the production of fine or various research chemical. Its industrial applications are now largly in the field of drug and perfume synthesis.
- **Medicinal Application**
    - Grignard reation is a vital step for the production of Tamoxifen (currently used for the treatment of estrogen receptor positive breast cancer in women).

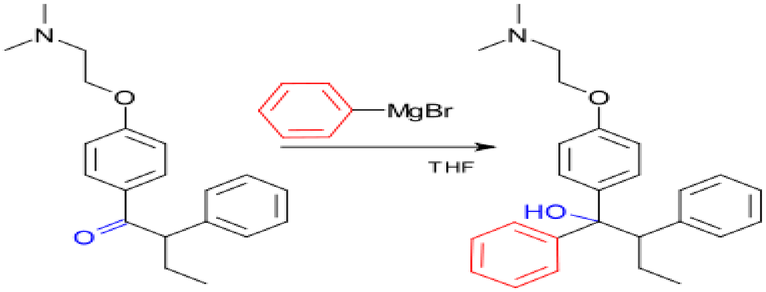


Figure 2.5 Tamoxifen Production

2.6.1 General Applications

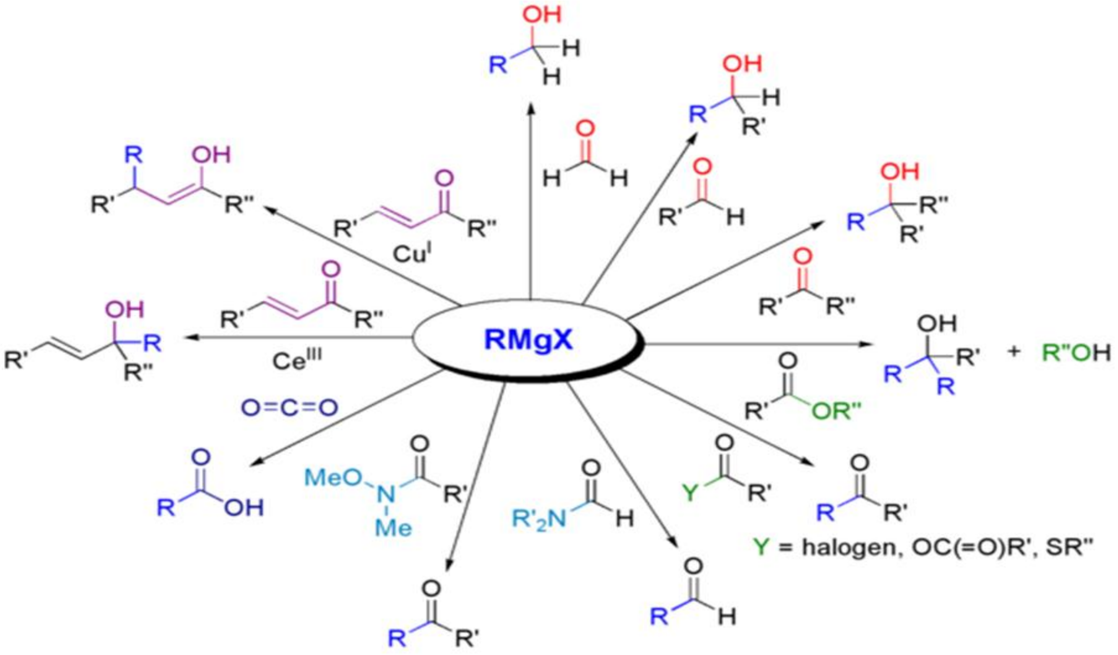


Figure 2.6 Reaction of Grignard reagent with different carbonyls

2.7 Reduction of Carboxylic Acids:-

2.7.1 Reduction Reaction:-

"The reaction in which any substance gains at least one electron and results in the reduction of its oxidation number is called Reduction reaction."

Or

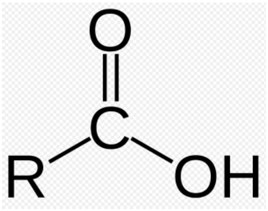
"Addition of Hydrogen or electron is Reduction"

2.7.2 Carboxylic Acids:-

"Carboxylic acids are the organic acids characterized by the presence of at least one carboxyl functional group."

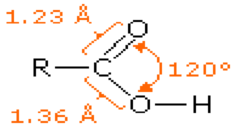
General formula for carboxylic acid is **R—COOH**,

Where **R** represents the alkyl or aryl group or any other



Structure of Carboxylic acid

mono-functional group and **–COOH** is the carboxyl functional group. Carboxy or carboxyl group is consisting of two functional groups. One is carbonyl group (C=O) and other is hydroxyl group (C—OH). These both groups on combination form carboxyl group which is usually written as –COOH or $–CO_2H$.



Carboxylic acids are the most common type of organic acids. They are Lowry—Bronsted acids as they can donate a proton (H^+). Among the simplest examples is formic acid (H--COOH) that occur in ants and acetic acid that gives sour taste to vinegar

2.7.3 Reduction of Carboxylic Acid:-

Carboxylic acid is composed of two functional groups. So, there is possibility of reduction reaction to proceed in two ways.

In case of carboxylic acid there are two possible reduction products:

- Aldehyde
- Alcohol

We need selective methods for selectively accessing either product.

2.7.4 Mechanism of Reduction Reaction:-

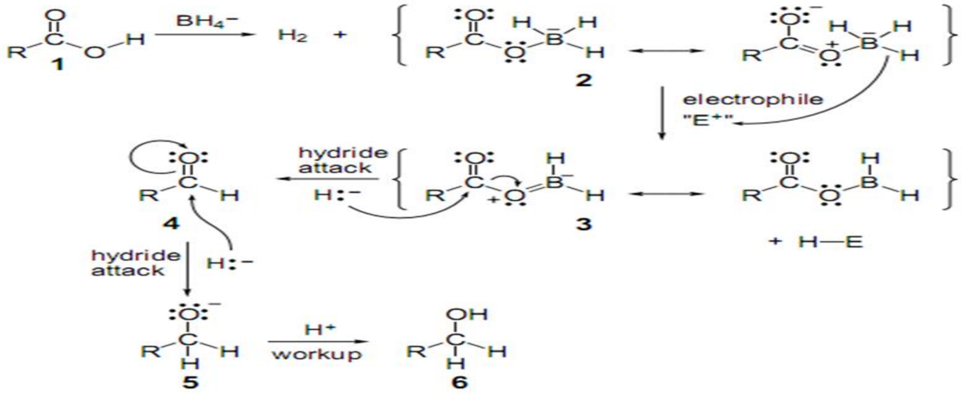


Figure 2.7 Probable mechanism of reduction

2.7.5 Reducing Agents:-

"A reducing agent is an element or a compound in reduction-oxidation reaction that donates an electron to another species."

Reducing agent is also called **Reductant** or **Reducer**. The reducers are oxidized within the reaction, as the reductant reduces an electron during the reduction reaction.

There are numerous varieties of reducing agents differing principally in their reactivity. They all act as a source of nucleophilic hydride and therefore are most reactive towards electrophilic species.

Some of the classes of reducing agents are discussed below,

1) **Hydrides Reducing Agents**
    - Lithium Aluminum Hydride **($LiAlH_4$)**
    - Sodium Borohydride**($NaBH_4$)**
    - Sodium Borohydride-Cerium (III) Chloride (using 1:1 ratio of **$NaBH_4$** and **$CeCl_3$**)
    - Sodium Cynoborohydride (**$NaCNBH_3$**)

2) **Neutral Reducing Agents**
    - Borane (BH_3)
    - Diisobutylaluminium Hydride (**DIBALH**)
    - Meerwein-Ponndorf-Verley Reduction with **$Al(OiPr)_3$**
3) **Stereoselective Reduction of Prochiral Ketones**
    - Diasteroselective formation of Anti-1,3-Diols
    - Diasteroselective formation of Syn-1,3-Diols
    - Diasteroselective formation of Anti-1,2-Diols
    - Diasteroselective formation of Syn-1,2-Diols
4) **Other Methods of Reduction**
    - Raney-Nickle
    - Zinc in Acidic Media
    - Hydrogenation with Hydrogen and a Transition Metal Catalyst

5) Dissolving Metal Reduction (Sodium/Ammonium or Lithium/Ammonium)

- Regiospecific Enolate Formation
- Birch Reduction
- Reduction of Alkynes
- Free Radical Reduction

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Gyeongsang National University, Chinju 660-701, Korea
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Chapter 3

Experimentation:

3.1 Grignard Reagent (RMgX) Preparation:-

Following are the chemicals required for the preparation of Grignard's Reagent which would be further utilized in the utilization of Carbon dioxide for the production of acetic acid as an essential chemical in our daily life as well as industrial applications

1. Magnesium turnings by **Merk**
2. Alky halide (Methyl bromide) by **BDH**
3. Diethyl ether by **SigmaAldrech**

Experimental work:-

For the preparation of Grignard reagent then above mentioned reagents were utilized. For experimental purpose it was essential to use mechanically activated Magnesium turnings instead of Rieke magnesium which is highly expensive and reactive towards air as well and dry ether. For that reason separate procedures were used.

3.1.1 Dry/Anhydrous Diethyl Ether Preparation:-

1. Diethyl ether, Ethyl Ether or Ether with chemical formula $(C_2H_5)_2O$
2. Nitrogen gas (N_2) for inert atmosphere
3. Sodium hydride (NaH)

Distillation:-

Distillation is a process to vaporize, recondense and then collect the liquid sample from the mixture or impure state of that liquid. Distillation is a method to purify a solvent from its impure form. The liquids have different volatilities that describe the relative ease with which the molecule of a specific solvent escape from the surface. It is opposite to the boiling point of a liquid. So, higher the volatility of a liquid lower will be its boiling point. Vapor pressure is the pressure exerted by a liquid on its pure state in a closed container at a specific temperature. It is a force that a liquid molecule exerts on a surface to escape. General trend for vapor pressure and boiling point represents that the vapor pressure of the liquid at ambient temperature increases with decreasing boiling point (Figure 3.1)[1]. Liquid will give off molecules, until the vapor pressure above the liquid become equal to the respective temperature.

When the solvent is enclosed, the liquid will evaporate until the vapor pressure of the gas above the liquid equals the vapor pressure of the liquid. If some of the gas vapor is removed, more liquid will evaporate in order to equalize the vapor pressure and partial pressure. This is the principle behind distillation [2].

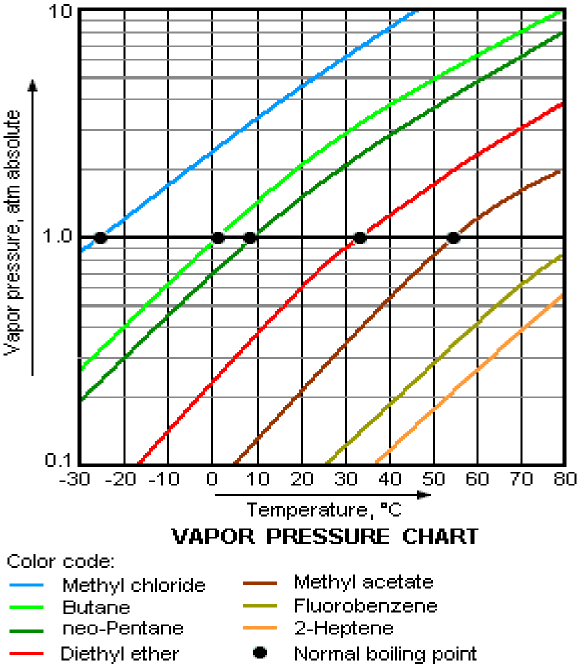

Figure 3.1 Typical vapor pressure chart for various liquids [1]

The impure liquid is heated in a distilling flask. The temperature of the liquid will rise (specific heat) till the temperature/vapor pressure or boiling point of the required liquid is reached. At this temperature all the heat energy given to the liquid is used to evaporate the liquid (heat of vaporization). The hot vapors of the desired liquid travels to the condensing column in upward direction were they are recondensed to the pure liquid state by removing the heat from the hot vapors. So, the hot gaseous vapors recondenses back to the liquid and is collected in the receiving flask. As it reduces the vapor pressure over the liquid in the distilling flask more liquid is converted to the liquid phase to equalize, which again recondenses. That is the general idea behind distillation method. In case of impure liquid the impurities will stay behind in the distilling flask and the pure liquid will be collected in the receiving flask.

Procedure:-

Take a 250ml three necks round bottom flask. To one neck of the flask fit the assembly for nitrogen atmosphere, as we have to prevent the contact of dry ether with air and moisture. Add 100ml Diethyl ether to the flask. To this flask with solvent add 10 to 15 grams of sodium hydride (NaH). Effervescence will start as NaH would be added. Now place the flask over the heating mentle and fit that flask with a distillation condenser and the next end of the condenser was having a collecting flask to receive the distilled product i-e Dry Ether. The collected dry ether was then placed in an air tight bottle to avoid its connection with the air or moisture.

Nitrogen cylinder Distillation Assembly

Figure 3.2 Distillation setup for the production of Dry Ether

3.1.2 Mechanical Activation of Magnesium Turnings:-

The mechanism for the formation of Grignard's Reagent needs a highly efficient and reactive magnesium metal surface as for the reaction of organo halides with magnesium it is vital that the electron should move from metal surface (magnesium) to the halide that would result in the formation of organo radical R• (alkyl radical). The Carbon (C) from radical R• (alkyl radical) bonds to the Magnesium metal and the recombination of this bonded specie with halide ion leads to the formation of RMgX, Grignard's reagent.

This is all possible when the reactive surface of magnesium is available to the reacting alkyl halide. Magnesium is not found naturally in a free or atomic state as it is highly reactive, once formed and exposed to air or moisture it quickly forms an oxide layer which partially mask the reactivity of magnesium metal. In air magnesium metal forms a hard inert surface naturally. This causes the passivation of magnesium metal. So it is important to activate the passive surface of magnesium to make it reactive for alkyl halide.

Required Chemicals:-

1. Magnesium turnings
2. Bromine
3. Argon (to create the inert atmosphere)

Procedure:-

Put 5grams of magnesium turning in 10 ml glass vial along with a magnetic stirrer. Add 3 to 4 drops of bromine (Br_2) to the turnings and close the vial with a septum to prevent any contact of air or moisture with the turnings. Insert a syringe connected to the argon cylinder to provide an inert atmosphere to the setup. Now place the vial on the stirrer and allow it to stir it for 2 days. The change in color from silver to dark gray indicates the activation of magnesium metal surface.

Figure 3.3 Activated magnesium turnings

3.1.3 Preparation of Grignard’s Reagent:-

Grignard’s Reagent is prepared by the reaction of alkyl halide with reactive magnesium in the presence of dry ether, Tetrahydrofuran (THF) or toluene.

Required Chemicals:-

1. Dry ether (Solvent)
2. Methyl Bromide, CH_3Br (Alkyl Halide)
3. Activated Magnesium
4. Iodine (initiator)

Reaction Conditions:-

It is imperative that the equipment and reagents used for the production of Grignard’s reagent must be properly dry and must not have any traces of water. Therefore the glass ware to be used in experiment must be dried by placing them in oven at 110℃ one lab period before starting the experiment. The magnesium turning must also be dry and can perform better if they are also placed in an oven before use. Rinse every glass ware and equipment with Dry or anhydrous ether before use. Prefer to use unused syringes and needles for experiment so that the chance of moisture contact can be minimize. Use silicon septum to minimize atmospheric contacts. It’s much preferable to conduct the experiment under Nitrogen or Argon atmosphere by applying air-free techniques.

Procedure:-

Take an oven dried reaction tube and place a small magnetic stirrer in it. Directly cover it with silicon septum to inhibit the entry of moisture into the oven dried reaction tube. Do not open or remove the septum excessively. Add 2 mmol (50mg) of activated magnesium turnings along with few crystals of iodine, just to initiate the reaction of methyl bromide with magnesium turnings (Figure 3.4). Place the silicon septum back at the tube. Using a dry syringe and needle add 0.5 ml of anhydrous diethyl ether (Figure 3.5).Take a short glass vial (oven dried). Add 2.1 mmol of methylbromide (0.7 ml) and 0.5 ml of dry ether. Straightaway with the same syringe remove all the solution from the vial and pour it into the reaction tube.

Figure 3.4 Magnesium turnings placed in the reaction tube

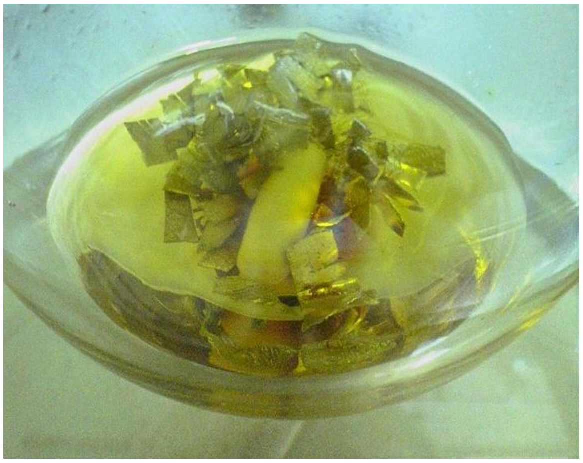

Figure 3.5 Mg turnings covered with anhydrous ether and piece of iodine

The reaction will not start in the beginning but by rubbing the base or bottom of the reaction tube with fingers the temperature of the reacting species will raise and the magnesium metal in the presence of iodine will react within seconds to form Grignard's reagent. Continue to stir the reaction throughout using the magnetic stirrer. The clear solution upon reaction achieve a cloudy appearance as soon as the reaction begin (Figure 3.6).

Figure 3.6 Addition of Methyl Bromide solution

After some time the magnesium metal will be consumed and the reaction would stop, resulting in the production of required Grignard's Reagent. Some of the magnesium will remain unreacted at the bottom of the flask even at the completion of the reaction (Figure 3.7).

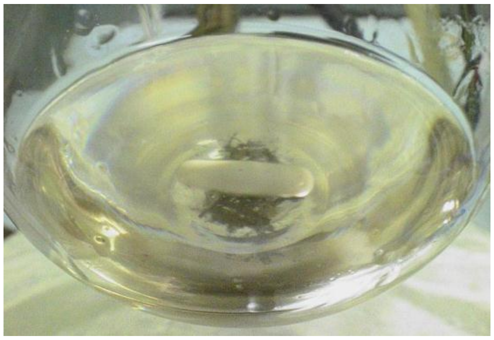

Figure 3.7 Complete formation of Grignard's Reagent

3.2 Utilization of Gaseous Carbon dioxide for the Production of Acetic Acid-

As soon as the Grignard's Reagent is formed it is to be reacted with the gaseous Carbon dioxide to produce acetic acid. As Grignard's Reagent is highly unstable specie so it is made to react with the Carbon dioxide through the syringe (Figure 3.8). The reaction is highly exothermic so the reaction tube was placed in the ice cool water. Allow the gaseous CO_2 to bubble through the solution for 15 min. The pressure relief was remained inserted into the septum of reaction tube to release the gaseous pressure from the reaction tube. The reaction of gaseous carbon dioxide with Grignard's Reagent produced Acetic acid which finally results into a clear solution in reaction tube (Figure 3.9)

Figure 3.8 Addition of CO_2 through syringe into Grignard's Reagent

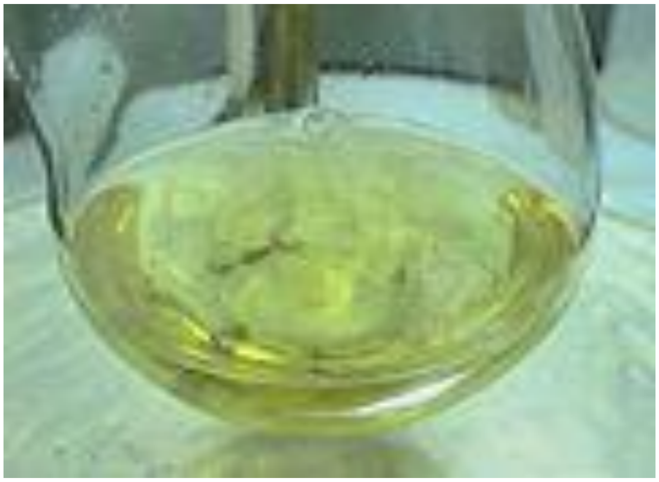

Figure 3.9 Final product

3.3 Working up for the Final Product:-

Required Chemicals:-

1. Hydrochloric acid (HCl) 3N
2. Diethyl ether (Ordinary)
3. Water
4. Sodium Hydroxide solution (NaOH)

Procedure:-

Take the final product sample from the reaction tube and add 2 ml to 3 ml of 3N hydrochloric acid. The addition of hydrochloric acid will neutralize the intermediate bromo salts formed during the reaction. Close the reaction tube and shake the mixture scrupulously. Allow the mixture to stand for few seconds. The mixture will form two homogenous layers. The aqueous layer is to be removed and the remaining ether layer was mixed with 2ml to 3 ml of water. Again remove the aqueous layer. Acetic acid is to be extracted by treating the ether layer with 1ml of 3M sodium hydroxide solution. Shake the mixture thoroughly and remove the aqueous layer and collect that aqueous extract into a small vial. Repeat the same extraction procedure for acetic acid using 3M sodium hydroxide and collect the aqueous extract in the same vial that was having the extract of first step. Final extraction step was carried out using 1ml water. The ether solution remaining in the reaction tube will have the bi products formed during the production of methyl magnesium bromide (CH_3MgBr).

The aqueous extract was heated at 50℃ within the same vial for few minutes so that any ether left during extraction can evaporate from the aqueous extract. Little amount of this extract was put into a 2 ml glass vial and few pinches of Sodium sulphate (Na_2SO_4) was added to it as it works as inert drying agent. The solution was shaken vigorously and allowed to settle the liquid was then filtered using micro filter and then the sample was ready for further analysis using High performance liquid chromatography (HPLC) and Fourier transform infra-red spectroscopy (FTIR).

3.4 Reduction of Acetic Acid to Produce Ethanol:-

Different methods were used for the reduction of acetic acid with different conditions. The methods along with their required chemicals and conditions are discussed as under.

3.4.1 Reduction of Acetic Acid using Sodium Borohydride ($NaBH_4$) with an Electrophile I_2:-

Four grams of Sodium Borohydride ($NaBH_4$) was added to a dry three neck round bottom flask. To this flask 50 ml Tetra hydrofuran was added. This suspension was allowed to stir for 10 mints so that a cream color suspension was formed. To this suspension 2.5 ml of acetic acid was added and then the solution was stirred for few mints. A solution of 10.6 gm of iodine (I_2) in 10 ml THF was added drop wise into the earlier formed suspension of $NaBH_4$, acetic acid and THF on an ice bath. The gas was allowed to release from the mixture and then this round bottom flask was fitted with the reflux condenser and was allowed to reflux for 2 hours.

After fefluxing the solution was allowed to cool at room temperature. Then 50 ml methanol was added to it and this solution was again reflux for 1 hour. After 1 hour the solvents (THF and methanol) were evaporated using rotary evaporator. The rotary evaporator was operating under vacuum at 40°c temperature and 80 revolutions per minute. The evaporation was continued till 2-3ml of mixture was left in the flask. 40 ml of 20 % KOH solution was added to the mixture was again refluxed and stirred for 2 hours. Now to collect the product formed, the mixture of again evaporated by using rotary evaporator operating under vacuum at 60°c and 80 revolutions per minutes. The expected product formed was having boiling point of 78.7°c so it will be collected in collecting flask first. From the collecting flask the product was transferred to a small vial and was further dried using Sodium sulphate (Na_2SO_4). The product sample was then analyzed using HPLC and FT-IR.

3.4.2 Reduction of Acetic Acid using Sodium Borohydride ($NaBH_4$) and Hafnium Tetrachloride ($HfCl_4$) under Mild Conditions:-

Freshly distilled THF (15 ml) was pour into a dry 2 neck round bottom flask with a magnetic stirrer, $HfCl_4$ (1.6 g, 5 mmol) , and $NaBH_4$ (0.75 g, 20mmol) were added to the flask and was stirred in an ice-water bath under nitrogen atmosphere. The mixture was stirred for 6 to

8 mints and a cream-colored suspension was formed. The suspension was warmed to room temperature for 2 hours. In another vial 0.5 ml of Acetic Acid was added to 10 ml THF. This mixture was then added drop wise to the stirred suspension of $HfCl_4$, $NaBH_4$ and Dry THF. This suspension was then stirred for 6 to 7 hours till the reduction of Acetic acid is completed. Then the final product or the reaction mixture was further processed for purification.

Processing / Work up Steps:-

The reaction mixture was poured directly into distilled water (5 ml), provided with ice cooling and extracted with ethyl acetate (5 × 5ml). The combined extract was washed with $NaHCO_3$ and brine (concentrated aqueous solution of NaCl). The final extract was then dried over anhydrous Na_2SO_4.

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A.S. Bhanu Parsad, J.V. Bhaskar Kanth and Mariappan Periasamy* School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

(Tetrahedron Vol. 48, No. 22, pp. 4623-4628, 1992)

Chapter

4

Analytical Techniques:

The reaction mixtures or the product formed after the reactions were completed were then analyzed by various Chemical analysis techniques just to confirm the production of expected product and to analyze the final product formed. For this reason different analytical techniques were utilized including;

- High Performance Liquid Chromatography (HPLC)
- Fourier Transform Infrared Spectroscopy (FTIR)

4.1 High Performance Liquid Chromatography (HPLC):-

High performance liquid chromatography sometimes referred as High-pressure liquid chromatography, HPLC, is a chromatographic technique used to separate the mixture of compounds in analytical chemistry and biochemistry with the purpose of identifying, quantifying and purifying the individual component of the mixture [1].

High performance liquid chromatography is the most self-motivated and active analytical technique. It is a separation technique involving mass-transfer between stationary and mobile phase. Different component of a mixture can be separated and purified by the help of HPLC. High performance liquid chromatography has attained a high grade of versatility which is not found in other analytical techniques as it has the ability to separate wide variety of chemical mixtures. There are two phases that are playing the major role for the separation of analyte or required sample through HPLC

1. Stationary phase, sorbent (immovable or immobile phase)
2. Mobile phase (Movable phase)

Stationary phase can be liquid or solid. It can be defined as the immobile packing material in the column. Mobile phase is a liquid that separates the components of a mixture by passing it through the column or stationary phase.

Figure 4.1 High Performance Liquid Chromatography

4.1.1 Principle of HPLC:-

The reaction mixture or the analyte is separated or purified because of the interaction of mobile and stationary phases. Analyte molecule interacts with the surface adsorption sites while passing through the column. And depending upon these interactions the components or analyte elute from the column and have different retention times.

There are different kinds of interactions that define the retention time of different analytes between the mobile and stationary phase. Depending upon the type of the column packing, the interaction strength varies. Analytes are separated through the column on the bases of various separation modes. Availability of these separation modes enhance the range of application of HPLC for chemical analysis.

Table 4.1 Examples of some HPLC column types and their operational interaction

Type of column	Mode of separation
Reversed / Normal phase	Difference in hydrophobicity (polarity)
Ion exchange	Difference in charge at a certain pH
Gel filtration	Difference in size (molecular weight)
Bio-affinity	Difference in interactions with a ligand

4.1.2 Types of HPLC:-

HPLC can be classified into different types depending upon the type of stationary phase and on the bases of separation process by which the analyte molecule is separated through the column. Some of the modes of HPLC can be specified.

a) Adsorption Chromatography:

Type of chromatography in which the stationary phase is a solid adsorbent mainly silica or any other silica based packing. The analyte is separated on the bases of repeated adsorption and desorption steps. Eluent polarity plays an important role in all types of HPLC. Depending upon the type of solid stationary phase the adsorption chromatography is further classified into two categories.

1. Normal phase chromatography: where the stationary phase is polar in nature and the mobile phase is non polar in nature. The polar samples will have longer retention time as compared to non polar analytes in case of normal phase chromatography.
2. Reversed phase chromatography: it is the inverse of normal phase chromatography, where the stationary bed is non polar and the mobile phase is highly polar. Here the more non polar the material is, the much longer will it stay in the column.

   Reverse phase chromatography plays an important role for the chemical analysis. It is used for almost 90% of all chromatographic applications.

b) Ion-exchange Chromatography:

It is the type of chromatography in which the stationary phase is an ionically charged surface. The charge of the surface or column is opposite to that of analyte. Stronger the charge on the stationary phase stronger will be the interaction between analyte and a column packing. So, the analyte will take longer time to elute out of column.

c) Size Exclusion or Gel filtration Chromatography:

Size exclusion chromatography is the type of chromatography in which the column is packed with precisely controlled pore size. The sample or analyte is filtered or screened through the porous column according to its molecular size. Large molecules leave the column first while smaller molecules enter into the pores of the column and stay there for long and elute out of the column with longer retention time. This technique is also known as **Gel permeation chromatography.**

d) Affinity Chromatography:

Affinity chromatography is basically used for biological specimens and that’s the reason that it is also known as **bio-affinity chromatography.** It is based on highly specific biological interactions such as that between antigen and antibody, enzyme and substrate, or receptor and ligand.

e) Chiral Chromatography:

Chiral chromatography involves separation of stereo isomers as conservative chromatographic techniques are incapable of separating them. For Chiral chromatography either the stationary phase or mobile phase must themselves be made chiral so that the analyte can show different affinities or interaction between them.

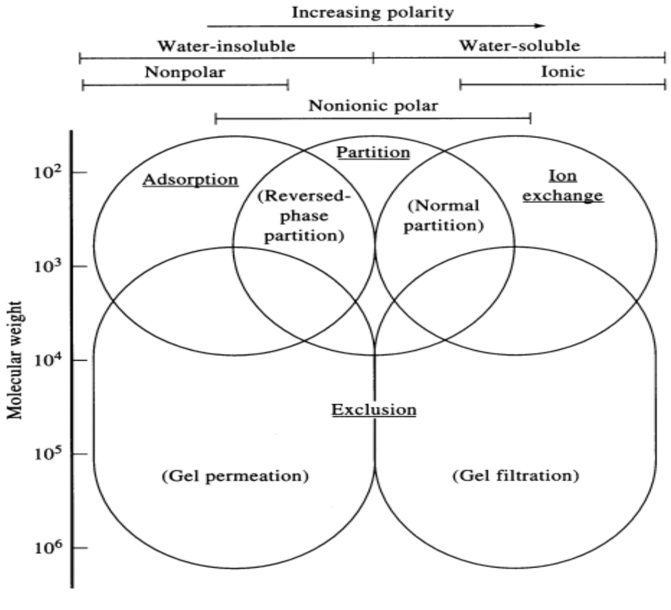


Figure 4.2 Applications of Liquid Chromatography [6]

4.1.3 Construction and Working of HPLC:-

The basic components of HPLC include

- Solvent reservoir

- Degassing system
- Pump
- Sample injection system
- Precolumn
- Column
- Temperature control
- Detector
- Recorder
- Waste reservoir

HPLC starts with a **solvent reservoir**, that contains the solvent (mobile phase) that carry the sample through the column. To protect the column and to make it functional for longer time duration it is preferable to use properly filtered solvent and analyte solutions so that any particles or impurities that can damage the column or system may be removed before utilization. Microfilters or microporous membranes are being in use for this purpose. Mobile phase is propelled into the column (stationary phase) by **pump**.

The sample or analyte is introduced through **sample injector** or **injection valve**. This valve is equipped with sample loop of appropriate size that allows suitable quantity of sample to flow into the column for analysis. It is essential to use minimum amount of sample as it contain various particulate matter, so to prevent this particulate matter to damage the system's sensitive parts it's advisable to use minimum quantity of sample and it's preferable to pass it through **sample filter** or precolumn filter.

Next is the **analytical column** or stationary phase of HPLC. The separation occurs at this point where the mobile phase and analyte flow through the column and are eluted with different retention times depending on their different interactions towards the stationary column packing. A sacrificial **guard column** is often used prior to the analytical column just to chemically remove the components that would otherwise foul the main analytical column. Following the analytical column is the **detector** that detects the specific characteristic response of sample towards the detector. Samples are characterized, analyzed, purified depending upon their responses towards specific detectors. The analyte component's presence in the column flow promotes an electrical response from the detector which is digitized and sent to **recorder**. Recorder analyzes and interprets the data. A **back pressure regulator** is often present within the HPLC equipment immediately after the detector. This helps to prevent the formation of solvent bubble formation until the solvent is completely passed through the column. It is important to avoid bubble formation in flow cell or column because these bubbles will interfere with the detection of sample component. The mobile phase after passing through the column is collected in **waste reservoir**.

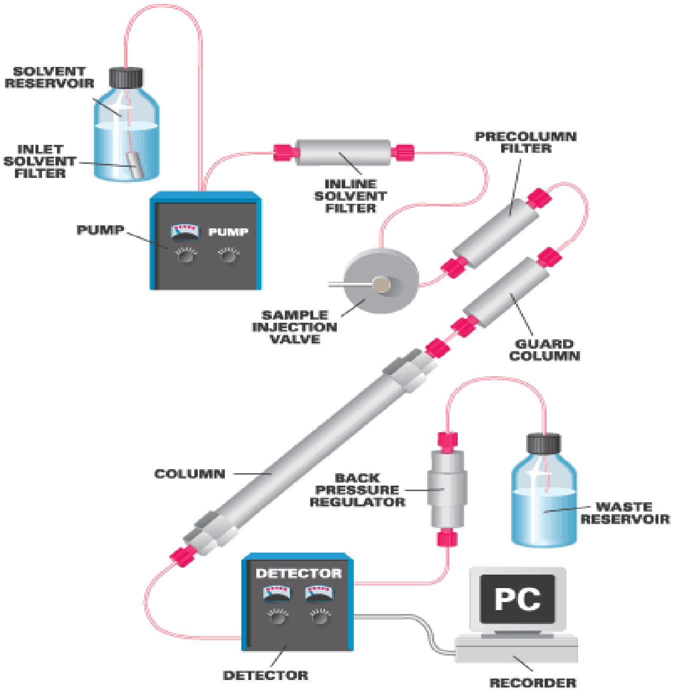


Figure 4.3 Diagrammatic presentation of HPLC [2]

4.1.4 Mobile Phases for HPLC:-

Different mobile phases or the solvents are used in HPLC technique for the analysis of wide range of chemical analytes. Type and composition of eluent (mobile phase) is the important factor controlling the separation. For the solvent to be used in HPLC there are certain properties that must be present within the solvent like purity, detector compatibility, solubility of the sample, low viscosity, chemical inertness. Some of the HPLC technique's mobile phases are:

Table 4.2 List of some mobile phases for HPLC

Sr No.	Mobile phases
1	Hexane
2	Toluene
3	Trichloromethane
4	Dichloromethane
5	Ether
6	Ethyl acetate
7	Acetonitrile
8	Methanol
9	Water

4.1.5 Stationary Phases for HPLC:-

Column packing or the stationary phase for HPLC strongly define the type of analyte to be separated and kind of mobile phase to be used. Different types of stationary phases available for various types of analytes are

Table 4.3 Stationary phases for HPLC and their applications

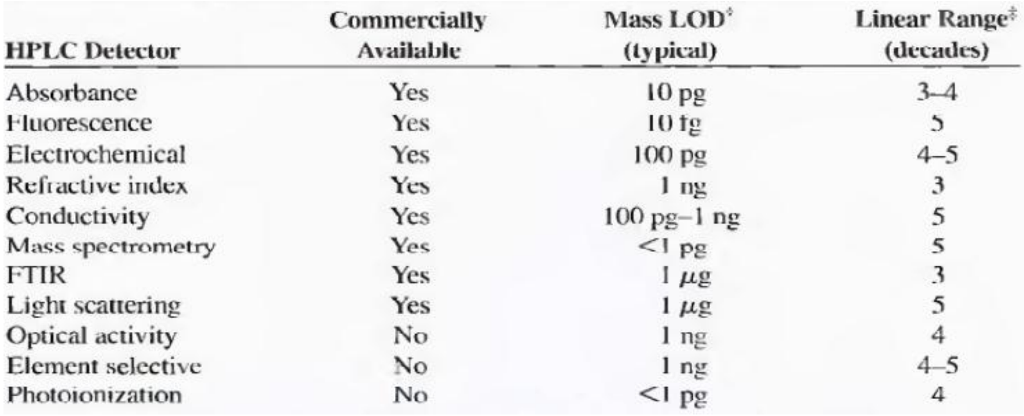
Stationary Phase	Application
C18	Pharmaceuticals, vitamins, amino acids, peptides, basic compounds, general purpose phase
C8	Proteins, peptides, estrogens, general purpose phase
C4	Biological separations, polar compounds, proteins
Phenyl	Phenol, fullerenes, sweeteners
Trimethyl silane	Water soluble vitamins

Diol	Polar natural products, pharmaceuticals
Amine	Saccharides, nucleotides, water soluble vitamins
Silica	Small organic molecules, fat soluble vitamins

4.1.6 Detectors for HPLC:-

Detectors operating at different principles are there for the sensing of solutes (analyte) in the mobile phase as it elute through the column. Theses detectors are of different types and are detecting a specific response for a specific analyte. Some of them are listed as under:

Table 4.4 HPLC detectors



HPLC Detector	Commercially Available	Mass LOD* (typical)	Linear Range‡ (decades)
Absorbance	Yes	10 pg	3–4
Fluorescence	Yes	10 fg	5
Electrochemical	Yes	100 pg	4–5
Refractive index	Yes	1 ng	3
Conductivity	Yes	100 pg–1 ng	5
Mass spectrometry	Yes	<1 pg	5
FTIR	Yes	1 μg	3
Light scattering	Yes	1 μg	5
Optical activity	No	1 ng	4
Element selective	No	1 ng	4–5
Photoionization	No	<1 pg	4

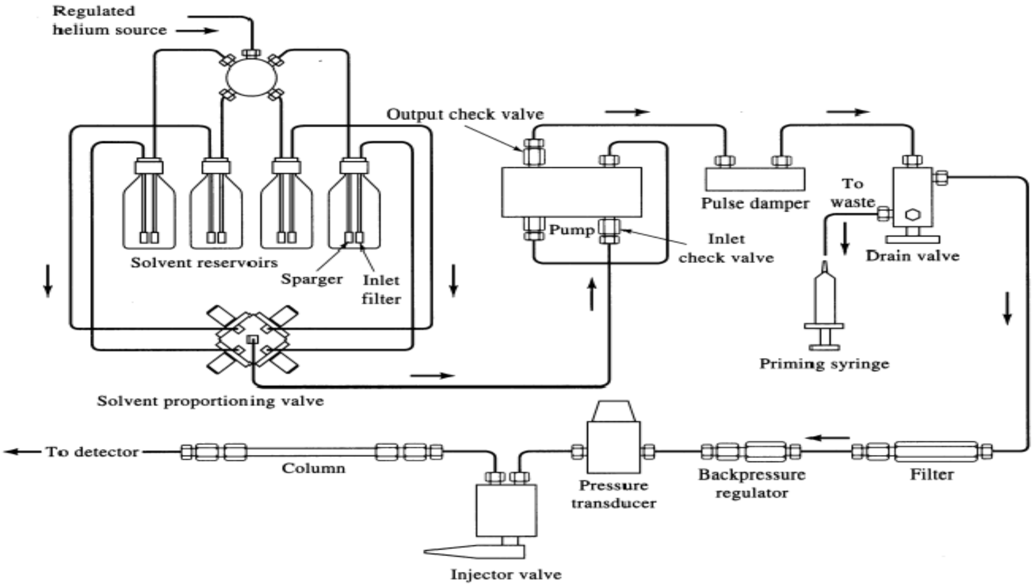


Figure 4.4 Flow sheet of HPLC [5]

4.1.7 Experimental Analysis:-

For the analysis purpose the analyte was Acetic Acid and Ethanol. Acetic acid was prepared by the reaction of Grignard's reagent with gaseous Carbon dioxide and the Ethanol was produced by the reduction of Acetic acid using Sodium Borohydride ($NaBH_4$) and any electrophile (I_2 in experimental workup) with varying conditions.

4.1.8 Parameters Utilized:-

For the analysis of acetic acid a phosphate buffer solution was prepared and was used as mobile phase. The phosphate buffer was having strength of 20 milimole and its pH was stabilized to 2.20 by using phosphoric acid. Acetic acid is weak acid and will ionize in any other mobile phase much faster. To reduce the rate of ionization and for accurate analysis it is advised to use buffer solutions as mobile phase for HPLC. The column used for analysis was C18 column and the detector was UV detector. Analysis was carried out at room temperature and the flow rate was 0.5 ml/min.

For Ethanol the mobile phase used phosphate buffer of 20 milimolar strength, whose pH was adjusted to 2.2 by using phosphoric acid. The buffered solution was filtered through 0.4 micron pore size cellulose membrane. It was used as mobile phase alone.

4.2 Fourier Transform Infra-Red Spectroscopy (FT-IR):-

FT-IR stands for Fourier Transform Infra Red Spectroscopy, one of the advanced and favorable methods of infrared spectroscopy. In this technique infrared radiations are passed through a sample. Some of the IR radiations are absorbed by the sample while rests of them are transmitted. These absorbed and transmitted radiations can produce an IR spectrum separately. These spectrums are known as absorption and transmission spectrum and they describe the molecular fingerprint of the sample. Like the fingerprints no two unique molecular structures produces the same infrared spectrum. This makes IR or FT-IR spectroscopy beneficial for different types of analysis.

Fourier transform infrared spectroscopy (FTIR) can provide clear information about the sample to be analysis. Like,

- It can identify unknown materials
- It can show the number of components within the mixture
- It is helpful in determining the quality and consistency of a sample (analyte)

FT-IR is preferred over the conventional IR spectroscopic techniques as it has overcome many issues that were present in older techniques like slow scanning process. In FT-IR a method was introduced for measuring all of the infrared radiations simultaneously rather than individually. A very simple optical devise was employed called **interferometer**. THE interferometer produces a distinctive signal which has all the infrared frequencies encoded into it. This signal can be calculated very quickly, usually on the order of **one second** or so. So FT-IR has reduced the time of sample analysis to seconds rather than several minutes. The resulting signal or the output of FT-IR is called **interferogram.**

Fourier transform infrared chromatography is preferred over conventional infrared spectral analysis for a number of reasons.

- It is non-destructive
- It has better optical throughput
- It is mechanically uncomplicated with only one part moving
- It provide a precise measurement method which needs no external calibration
- It can add to speed, collecting a scan every second
- It can amplify sensitivity

4.2.1 Sample Analysis Process:-

Following are the main components involve in the analysis of a sample at FT-IR. The FT-IR instrumental procedure is as follow:

(i) The Source:

The infrared radiations are emitted from a glowing black body source. These IR radiations pass through an aperture that allow the limited amount of radiation to the sample that will ultimately reach the detector.

(ii) The Interferometer:

The IR beam goes into the interferometer after passing through the aperture. Spectral encoding takes place at interferometer. The resulting interferogram signals then leave the interferometer.

(iii) The Sample:

The samples are held in the sample compartment in the form of KBr disc (if the sample is solid) or are placed on NaCl disc (if the sample is liquid). The beam enters the sample compartment and fall on the sample. From the sample surface either the beam is reflected or transmitted through the sample, depending upon the type of analysis being made. This is the point where the specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

(iv) The Detector:

The beam after passing through the sample teaches the detector for final assessment.

(v) The Computer:

The measured signal is digitized and is passed to the computer. Fourier transformation takes place at computer. Final infrared spectrum is now ready for reading.

In case of FT-IR there is need of a relative scale for the absorption intensity. For this purpose **background spectrum** must also b measured. Measurement without sample in beam is called background spectrum. This can be compared to the measurement with the sample in the beam to determine the beam to measure the Percent transmittance.

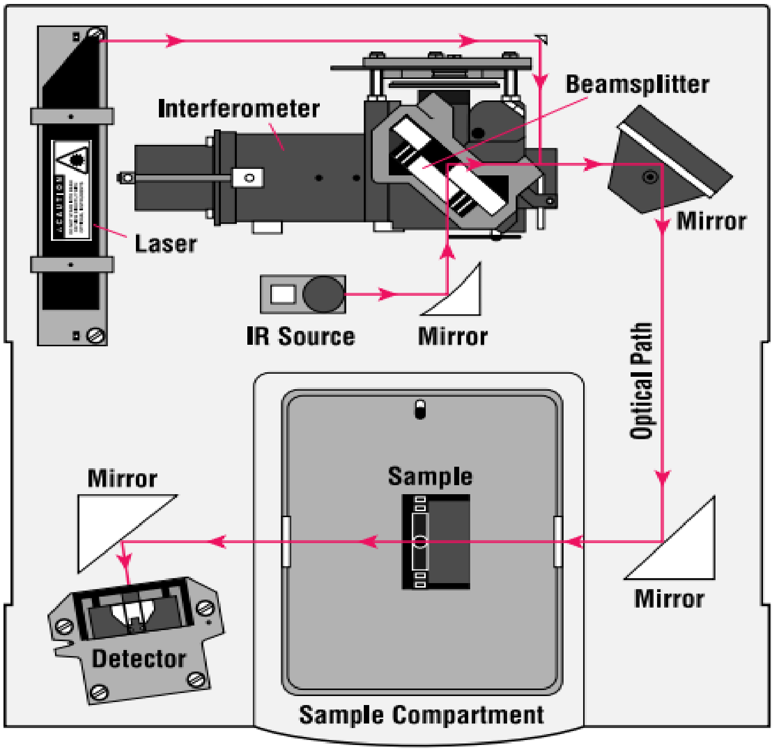


Figure 4.5 Simple FT-IR Spectrometer layout

4.2.2 Experimental Analysis:-

Sample to be analyze are acetic acid and ethanol. Both are liquid samples. Potasium Bromide (KBr) disc is used to hold the sample in sample compartment. Lithium Tantalate, $LiTaO_3$ was used as the source of radiation source and detector was used to analyze the sample. The analysis was made at room temperature and ambient atmosphere. The inerferogram was made for both sample and were read for further confirmations.

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[6] D.L.Saunders in Chromatography, 3rd ed., E.Heftmann, Ed., p.81.

New York: Van Nostrand Reinhold, 1975.

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Chapter

5

Results and Discussions:

5.1 High Performance Liquid Chromatography (HPLC) Analysis:-

Instrument Specifications:

HPLC model: Perkin Elmer series 200

Detector: UV detector

Column: C-18 ODS

Software: Totalchrome work station

Max pressure: 6200psi

HPLC present in chemical analysis laboratory is of Perkin Elmer model, series 200. It is equipped with C-18 column. This column can be used for wide range of analysis. C18 column is used worldwide as the most versatile stationary phase. Perklin HPLC instrument is equipped with UV detector. Column has small diameter so the volume of the sample or analyte to be introduced into the column is limited upto 20 microliter.

For Acetic acid analysis specific mobile phase was required as it is weak acid and can ionize easily. So, for that reason literature survey was made to find out the mobile phase for acetic acid analysis, and from the article "Usefulness of Organic Acid Produced by *Exiguobacterium sp.* 12/1 on Neutralization of Alkaline Wastewater" it was concluded that the phosphate buffer of pH 2.2 have 20 millimolar strength can be used as mobile phase for the analysis of organic acids including acetic acid. First step was to make the confirmation that the reaction product formed as the result of experiment was acetic acid. For this standard acetic acid peak and retention time was required so, first of all the mobile phase base line was set and then by using Phosphate buffer Solution of 20 milimolar strength (pH 2.2). The buffer solution was filtered through 0.4 micron pore size cellulose membrane before use so that all the particulate material can be removed so that it will not cause any damage to the sensitive parts of instrument like injection valve, HPLC column etc. Different standard solutions of acetic acid were prepared in HPLC grade water having acetic acid concentration of 20ppm, 40ppm and 60ppm. They were analyzed separately.

Table 5.1 Parameters for Acetic acid analysis by HPLC

Analysis parameters:	
Mobile phase	Phosphate buffer (pH 2.2)
Hplc column	C-18
Detector	UV
λ max	254
Flow rate	0.5 ml/min
Standby time	15 mint
Sample volume	20µl
Max pressure	6200 psi
Operating temp	Room temperature

The results of HPLC analysis are in the form of chromatograms showing the plot of detector response (y-axis) vs. time in mints (x-axis). The Standard solutions show the retention time of 1.05 min with the flow rate of 0.5 ml/min. The analysis run was made for 10 mints. The results are shown for a single sample (60 ppm).

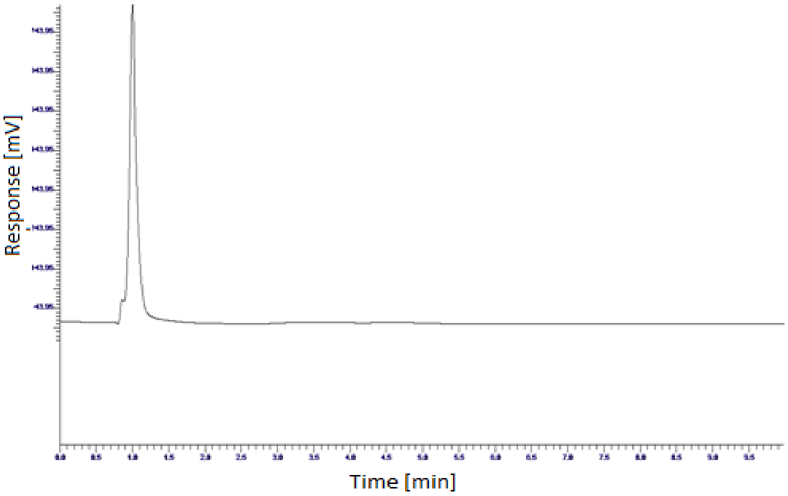


Figure 5.1 HPLC chromatogram for acetic acid standard solution

For the analysis of reaction product first the reaction product was filtered through a micro filter to remove any dust particles or any other particulate matter. Then using same analytical method as was used for standard acetic acid reaction was analyzed and it was seen that under same condition and parameters acetic acid peak was observed at the same location. Its peak was found at exactly same position where standard acetic acid was found. Its retention time was 1.00 mints.

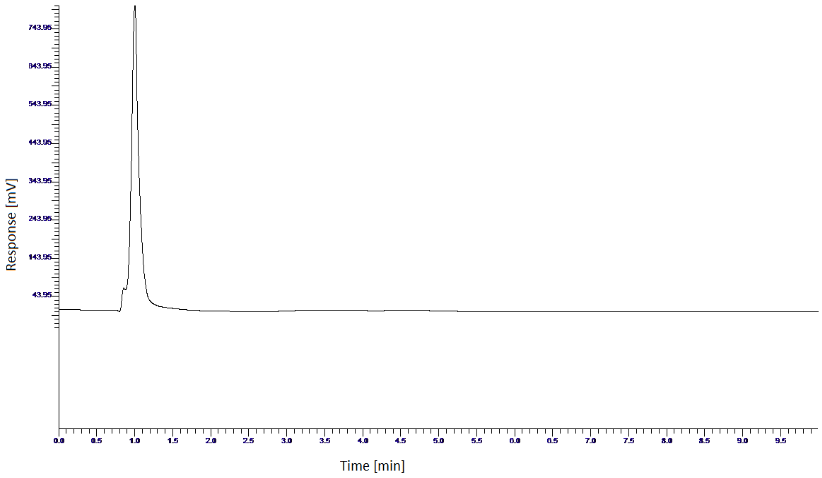


Figure 5.2 HPLC of acetic acid reactions product

This confirmed the formation of acetic acid by the reaction of Grignard's reagent with gaseous CO_2 .

5.2 Fourier Transform Infrared Spectroscopy, FT-IR:-

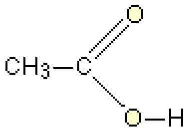
Instrument Specifications:

FT-IR model:	Spectrum series 100
IR source:	Lithium Tantalate, $LiTaO_3$
Response Measured:	Transmittance
Resolution:	$4cm^{-1}$

For the analysis of reaction mixture to confirm the formation of acetic acid it was essential to have the detailed chemical structure over view of Acetic acid. For this a standard acetic acid interferogram was recorded by placing the drop of sample on KBr disc and again covering the drop with another KBr disk. This disc was then placed on sample compartment and the FT-IR analysis was made. The interferogram is consisting of **fingerprint region** and **functional group** region. Fingerprint region describes the region that absorbs the wavelength due to all manners of bending vibrations occurring within the molecule. It ranges from 1500 – 500 cm^{-1}. This region is complicated one and is at the right-hand side of the spectrum. The region towards the left of spectrum is called the functional group region and describes the type of functional groups present within the molecule. It ranges from 1500 – 4000 cm^{-1}.

5.2.1 Acetic acid:-

As acetic acid has structure,



So, the FT-IR interferogram must contain following binds:

Carbon-oxygen double bond, C=O

Carbon-oxygen single bond, C-O

Oxygen-hydrogen, O-H

Carbon-hydrogen, C-H

Carbon-carbon single, C-C

Carbon-carbon bond has absorption in the range of wave number in fingerprint region. That's why it is difficult for one to analyze this peak. The carbon-oxygen bond also show an absorption wavelength in finger print region varying between 1000 and 1300 cm^{-1}. The carbon-hydrogen bond absorbs in the range from 2853 – 2962 cm^{-1}.

The most useful absorption bands for the analysis of acetic acid are by C=O and O=H bonds. C=O absorption is within the range of 1680-1750 cm^{-1}. The position of carbon-oxygen double bond may vary slightly depending upon the other compounds present with acetic acid. O=H bond is the most obvious and confirmatory absorption. It can be easily recognized in an acid as it produces a very broad trough on the interferogram in the range of 2500-3300 cm^{-1}. The standard FT-IR of the pure acetic acid was taken first so that the results of reaction product can be compared to that of standard for confirmation. The peaks of standard FT-IR should coincide with that of the reaction product to confirm that the acetic acid has been produced by the experiment. The useful peak range is:

Table 5.2 Table showing absorption frequencies of identifying bands for acetic acid

Type of bond	Wave Number Range (cm^{-1})
O-H	4000-3000 cm^{-1}
C=O	1900-1600 cm^{-1}
C-O	1300-900 cm^{-1}

FT-IR results for standard acetic acid are:

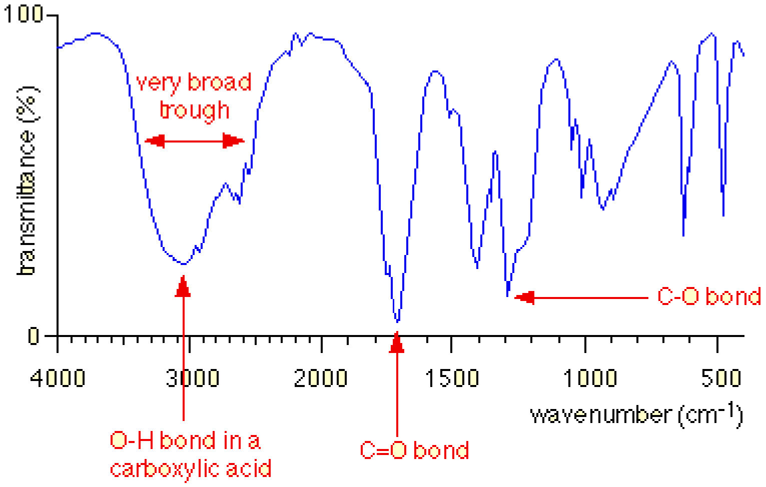


Figure 5.3 FT-IR spectrum of pure acetic acid (Ethanoic acid)

The results of reaction product sample at FT-IR are,

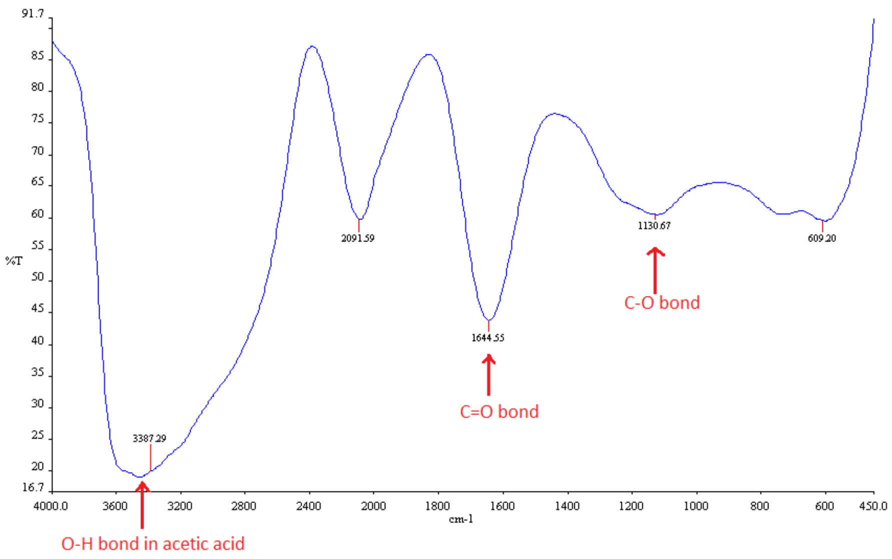


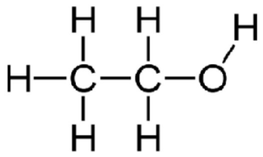
Figure 5.4 FT-IR spectrum of reaction's product sample (Expected to be acetic acid)

In figures i-e Figure 5.3 and 5.4, the peaks are shown to coincide with each other. It confirms the presence of same compound i-e Acetic acid, in both cases. It confirms the formation of acetic acid by our experimental work.

5.2.2 Ethanol:-

Our experimental work was aimed to prepare ethanol by reducing acetic acid using reducing agents. For this purpose different experiments were performed to form ethanol under varying conditions. For its analysis like acetic acid first it was essential to have FT-IR spectrum of pure ethanol that will work as a standard for our reaction product samples.

Ethanol has structure,



In case of ethanol, the useful frequencies are by,

Oxygen-hydrogen bond, O-H

Carbon-hydrogen bond, C-H

Table 5.3 Identifying frequencies for ethanol

Type of bond	Wave number range (cm^{-1})
O-H	4000-3000 cm^{-1}
C-H	2853-2962 cm^{-1}
C-O	1300-900 cm^{-1}

The FT-IR for pure Ethanol was made and the result obtained is,

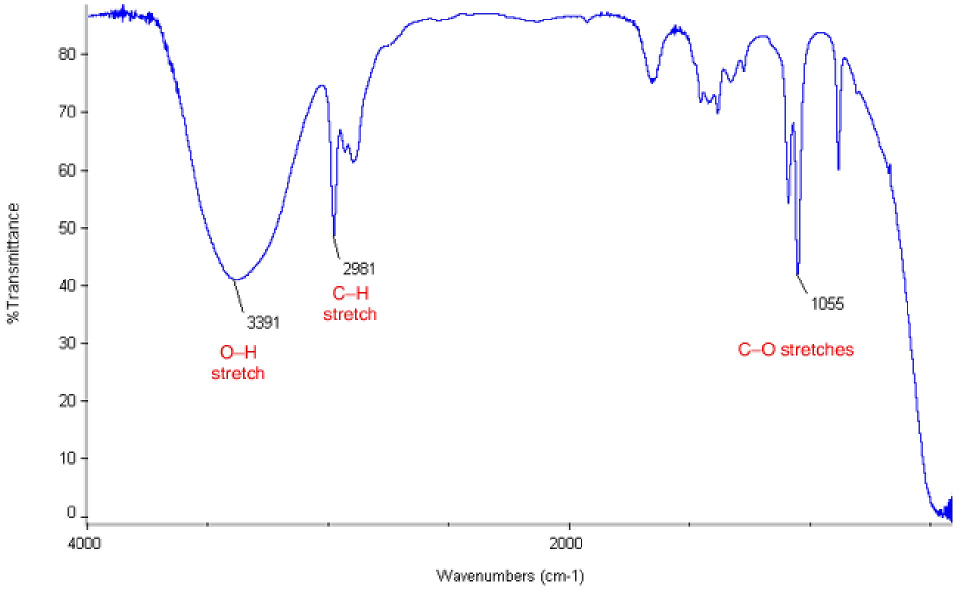


Figure 5.5 FT-IR result of pure Ethanol

FT-IR results of reaction's product sample 1 and 2 were also taken by the similar procedure as was used for pure ethanol so that the sample results can be compared to the standard of pure ethanol for confirmation. As we have used two methods for reduction of acetic acid so the results of both methods were analyzed.

The results of these experiments are:

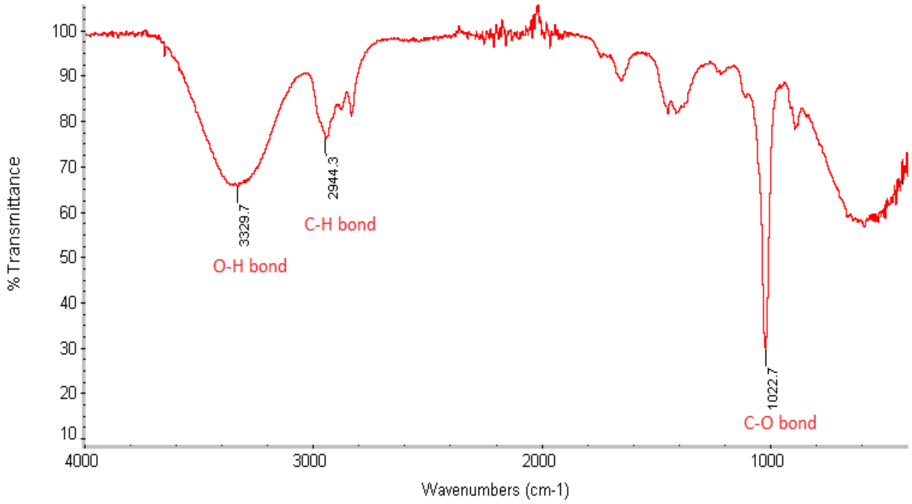


Figure 5.6 FT-IR results of reduction reaction using $NaBH_4$ in combination with an electrophile

The sample prepared by another reduction method was also analyzed. This reduction was carried out by using $NaBH_4$ and $HfCl_4$ as reducing agents. The result is;

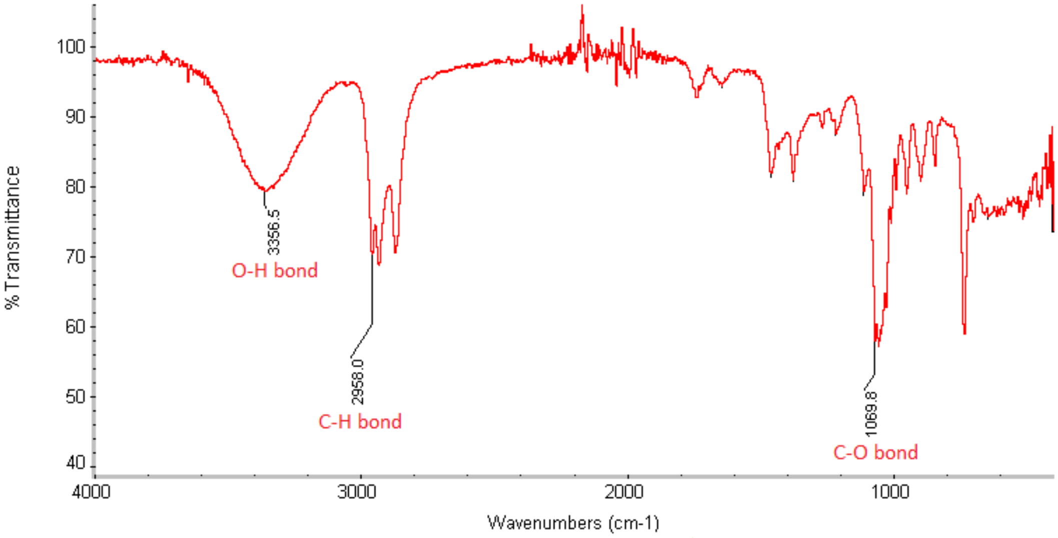


Figure 5.7 FT-IR results of reduction reaction using $NaBH_4$ and $HfCl_4$ as reducing agents

The FT-IR results of pure ethanol, sample 1 and sample 2 shows absorption due to O-H bond, C-H bond and C-O bond lying within the same ranges which confirms that the product formed by both reduction method is “Ethanol”

Among these two methods method 1 that produced sample 1 is much feasible and economical as the reducing agents used in this method are cheap and are easily available.

Conclusion:

The drastic increase in climatic issues regarding the gradual increasing concentration of CO_2 is resulting in the initiations of various means and ways to control this concentration. One of the techniques is to utilize the CO_2 in various methods as a raw material for the production of beneficial chemical compounds. This can be done by utilizing this dangerous greenhouse gas (CO_2) before releasing it into the atmosphere.

This research work was aimed at utilizing this waste CO_2 as a raw material for the production of useful chemicals like organic acids (acetic acid) and alcohols (ethanol). Here the CO_2 was used in gaseous form so that the processing of CO_2 can be minimized. The end products of the research work are Acetic Acid (CH_3COOH) and Ethanol (C_2H_5OH). These results were confirmed by High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared Spectroscopy (FTIR). The peaks of the products obtained from the experimental work were compared to that of the standards.

All the discussed results show that the acetic acid can be produce by reacting Grignard’s reagent with gaseous carbon dioxide (CO_2) and the acetic acid produced can be further reduced to ethanol by using different reducing agents working under different conditions.